SPECIATION AND BIOAVAILIBILITY OF RARE EARTH ELEMENTS (REEs) IN EX-TIN MINING AREA: A CASE STUDY FROM LAHAT, PERAK, MALAYSIA

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ABSTRACT

The main purpose of the study was to correlate the concentrations of rare earth elements (REEs), speciation and bioavailability. This study was proposed to investigate the distribution of REEs in abandoned mining land in Perak, Malaysia. Inductively coupled plasma mass spectrometry (ICP-MS) was used as major technique in this research. In this work, water, soil, sediment and plant samples were collected in the ex-tin mining area in Lahat, Perak, Malaysia in order to study the concentration, speciation, bioavailability and potential mobility of REEs. Water from ex-mining lakes and Kinta River was analyzed along with sediments. The results obtained revealed that the ex-mining lake water was found to be higher in REEs than that of the river water. The sediment samples were found highly accumulated with REEs. The analytical data obtained in this study was then analyzed using various chemometric methods such as principal component analysis (PCA), factor analysis (FA) and hierarchal cluster analysis (HCA). From the elemental analysis of ICP-MS, it is observed that soil samples taken from different depths in Perak were well separated into two clusters based on rare earth element concentrations and physical properties. The statistical analysis also indicated that REEs were the discriminating factors for the separation of soil samples at the depth of 0-20 cm from the rest. In addition, the samples taken from industrial and mining areas were clustered away from natural and residential areas, suggesting ex-mining and industries being the major source of REEs in the studied area. Different environmental impact assessments were done using enrichment factor (EF), geoaccumulation index (Igeo), contamination factor (CF) and pollution load index (PLI). Speciation study carried out for sediment and soil using sequential extraction procedures, indicate REEs mainly predominated in the adsorbed/exchangeable/carbonate fraction and in bound to silicates/residuals fraction while very small amounts of REEs were found bound to sulphides/organics and amorphous and crystalline Fe oxides. REEs were clearly separated into five fractions of

sequential extractions indicating their active mobility in the environment. The data obtained successfully measures the potential mobility of REEs and significantly describe higher for light rare earth elements (LREEs) rather than heavy rare earth elements (HREEs). Bioavailability of REEs indicate most of the plants as hyperaccumulators in their root and leaves parts while others accumulator and tolerant. Transfer factor (TF), bioconcentration factor (BCF) and bioaccumulation factor (BAF) analyzed were > 1 for hyperaccumulators, making them good phytoremediators for REEs. Based on the analytical method, chemometric techniques and environmental impact factors, it can be concluded that even though physical and chemical variables vary from sample to sample, distinct separation between samples from different areas of ex-mining land can be clearly observed.

ABSTRAK

Tujuan utama kajian ini adalah untuk menghubungkaitkan kepekatan unsur-unsur nadir bumi (REEs), penspesisan dan ketersediaan bio. Kajian ini telah dicadangkan untuk menyiasat taburan REEs dalam tanah lombong terbiar di Perak, Malaysia. Plasma pengkupelan aruhan - spektrometri jisim (ICP-MS) telah digunakan sebagai teknik utama dalam kajian ini. Dalam kerja-kerja ini, sampel air, tanah, sedimen dan tumbuh-tumbuhan telah dikumpulkan dalam kawasan perlombongan bekas timah di Lahat, Perak, Malaysia untuk mengkaji tumpuan, penspesiesan, ketersediaan bio dan potensi pergerakan REEs. Air dari tasik bekas lombong dan Sungai Kinta dianalisis bersama-sama dengan sedimen. Keputusan yang diperolehi menunjukkan bahawa sampel air tasik dari bekas lombong telah didapati mengandungi REEs yang lebih tinggi berbanding air sungai. Sampel sedimen didapati mengandungi kandungan REEs yang terkumpul. Data analisis yang diperolehi dalam kajian kami telah dianalisis dengan menggunakan pelbagai kaedah penganalisan kimia seperti analisis komponen prinsipal (PCA), analisis faktor (FA) dan analisis kelompok hireraki (HCA). Daripada analisis unsur ICP-MS, diperhatikan bahawa tanah yang diambil pada kedalaman yang berbeza di Perak yang telah diasingkan kepada dua kelompok berdasarkan kepekatan unsur nadir bumi dan ciri-ciri fizikal. Analisis statistik juga menunjukkan bahawa REEs merupakan faktor diskriminasi untuk pemisahan sampel tanah pada kedalaman 0-20 cm dari sampel yang lain. Di samping itu, sampel yang diambil dari kawasan industri dan perlombongan terletak di kelompok juah daripada kawasan semulajadi dan kawasan kediaman menunjukan bekas lombong dan industri sebagai sumber utama REEs di kawasan yang dikaji. Penilaian kesan alam sekitar yang berbeza telah dilakukan dengan menggunakan faktor pengayaan (EF), indeks pengumpulan geo (Igeo), faktor pencemaran (CF) dan indeks beban pencemaran (PLI). Kajian penspesiesan dijalankan untuk sedimen dan tanah menggunakan prosedur pengekstrakan berurutan, menunjukkan REEs terjerap / boleh tukar / karbonat pecahan

dan terikat kepada silikat / sisa pecahan manakala jumlah yang sangat kecil REEs didapati terikat kepada sulfida / organik dan amorfus dan hablur Fe oksida. REEs telah jelas dipisahkan kepada lima pecahan daripada pengekstrakan berurutan menunjukkan pergerakan aktif mereka dalam alam sekitar. Data yang diperolehi berjaya mengukur pergerakan potensi REEs dan ketara menerangkan lebih mendalam untuk unsur-unsur cahaya nadir bumi (LREEs) daripada unsur-unsur nadir bumi berat (HREEs). Ketersediaan bio REEs menunjukkan kebanyakan tumbuh-tumbuhan sebagai pengumpulan hiper dan meninggalkan bahagian di akar mereka manakala yang lain akumulator dan toleran. Transfer Factor (TF), faktor biokepekatan (BCF) dan faktor bio (BAF) dianalisis adalah > 1 untuk pengumpulan hiper, menjadikan mereka sebagai pemulihanfito yang baik untuk REEs. Berdasarkan kaedah analisis, teknik kemometrik dan faktor-faktor impak alam sekitar, boleh disimpulkan bahawa walaupun pembolehubah fizikal dan kimia yang berbeza dari sampel ke sampel, pemisahan yang ketara antara sampel dari pelbagai tanah bekas lombong boleh dilihat dengan jelas.

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LIST OF ABBREVIATIONS

AEC	Adsorbed Exchanged Carbonate
BAF	Bioaccumulation Factor
BCF	Bioconcentration Factor
m^3	Cubic meter
CEC	Cation Exchange Capacity
CV	Coefficient of Variation
r^2	Correlation Coefficient
C	Concentration
CF	Contamination Factor
DO	Dissolved Oxygen
°C	Degree Centigrade
EC	Electrical Conductivity
EF	Enrichment Factor
FA	Factor analysis
Igeo	Geo-accumulation Index
HCA	Hierarchical Cluster Analysis
HREEs	Heavy Rare Earth Elements
HR-ICP-MS	High resolution Inductively Coupled Plasma Mass Spectrometer

ICP-MS	Inductively Coupled Plasma Mass Spectrometer
IC	Ion Chromatography
INWQS	Interim National Water Quality Standards
Kg	Kilogram
LOD	Limit of Detection
LOQ	Limit of Quantification
LREEs	Light Rare Earth Elements
MC	Moisture Content
MREEs	Middle Rare Earth Elements
µg kg^{-1}	Microgram per kilogram
mg kg^{-1}	Milligram per kilogram
µg L^{-1}	Microgram per liter
µg g^{-1}	Microgram per gram
mm	millimeter
M	Molar
mL	Milli liter
µm	Micrometer
Min	Minimum
Max	Maximum
NIST	National Institute of Standards and Technology
OM	Organic Matter

PCA	Principal Component Analysis
ppm	Parts per million
ppb	Parts per billion
pmol kg^{-1}	picomol per kilogram
PLI	Pollution Load Index
REEs	Rare Earth Elements
REY	Rare earths Yttrium
REO	Rare Earth Oxide
rpm	revolutions per minute
SD	Standard Deviation
SRM	Standard Reference Material
SEP	Sequential Extraction Procedure
TSS	Total Suspended Solids
TOC	Total Organic Carbon
TDS	Total Dissolved Salts
TF	Transfer Factor
WHO	World Health Organization
XRD	X-ray Diffraction
XRF	X-ray Fluorescence

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CHAPTER 1: INTRODUCTION

1.1 Background of study

Most of the countries in the world exploit their natural resources in various activities to attain better economic conditions. In order to achieve such developments for any civilization, environmental sustainability become a critical encounter (Emerson et al., 2012, Kobayashi et al., 2014). An example of such activities is the mining that provides economic growth, worldwide trading, employment and better living cost to the nations endowed with mineral resources (Casper, 2007). Mining is not considered as permanent land use activity in temporal and spatial domain, therefore, it has become very crucial to predict accurately disorders. Demand of the metals mining for industrial purposes and to build infrastructure has increased due to urbanization, minerals availability, and government policies for economic advancement and world's population sprawl (Kobayashi et al., 2014, Swenson et al., 2011, Zhang et al., 2017).

Such demand has put a significant attention to solve social conflicts (Jeromino et al., 2015: Sudmeier-Reiux et al., 2015), mitigate highly sensitive and vulnerable land degradation at all scales (Andrew, 2003) and to maintain land (Malaviya et al., 2010, Barkemeyer et al., 2015). Today, all over the world environmental concerns due to mining activities in developing and mineral bearing countries have been widely raised. To rehabilitate and re-use degraded land, human resources, financial inputs, physical efforts would be doubled if such problems associated with mining activities are not held. Rare earth elements (REEs) are obtained as a byproduct in tin mining activities.

Lanthanide series include rare earth elements (REEs) with scandium (Sc) and yttrium (Y), being similar in chemical properties and deposited in ores same as REEs (Zdzislaw and Agnieszka, 2015, Khan et al., 2016). Rare earths are the elements with atomic number 57-71 including yttrium (39) and scandium (21), classified into two major groups i-e light

rare earth elements or Cerium group (LREE) and heavy rare earth elements or Yttrium group (HREE). Light REEs or Ce group contains La, Ce, Pr, Nd, Pm, Sm, Eu, Gd while Heavy REEs or Y group contains Y, Tb, Dy, Ho, Er, Tm, Yb, and Lu. LREEs are with atomic numbers 57- 62 and HREEs are with atomic numbers 63-71. Lu occurs more than gold and therefore information on their concentrations and distribution in the environment is important (Wedepol, 1995).

Tin is considered as oldest known metal to man. Until 2015, tins global production was about 335,000 tonnes of which 3-4 % cassiterite (SnO_2) contribute from Central eastern Africa (Barume et al., 2016). REEs are extracted as a byproduct in tin mining operations (Gupta and Suri, 1993). In the beginning of 19^{th} century, Malaysia become world's largest producer of tin and second largest producer and importer of REEs after China (Khan et al., 2016, Min, 2007). For many years, human activities have been a significant source of trace metallic elements eventually contaminating the earth's surface. Such actions overburdened the regime of ecosystem in aquatic and terrestrial environments with large quantities of trace metallic pollutants and contaminants.

1.2 Concentration, speciation and bioavailabilitiy of REEs

Rare earth elements (REEs) are not rare in true sense as the term indicate but are widely distributed in the earth's crust (Min, 2007). Mining activities in the specific area leave behind wastes that is transferred to the surrounding environment through different paths ways. In recent years, REEs have been of major concern to the researchers because of their unlimited applications in engineering and different technologies. Determination of REEs concentration, chemical form and mobility in different environmental areas has become of utmost importance (Khan et al., 2016).

REEs concentration for environmental study is not enough but two most considered characteristics are the speciation and bioavailability. Speciation is closely related to

mobility and toxicity of the metals and also some techniques for remediation (Adamu et al., 2013). Recently this technique has been of significant importance in many fields of chemistry because of a determination of distinct species in different chemical forms or the compounds in which REEs are mostly bound or present. The REEs fractionation is most consistent measures of hazardous effects of REEs in the sediment/soil and its consequence on other environments. For soil, it is very hard to find the real system for metal in which it is present (Hill, 1997).

Sequential extraction procedures (SEPs) for REEs speciation study in different environmental media have been more common (Guevara et al., 2004). The form in which REEs are present is more important to evaluate their toxicity. This is acknowledged as a useful method for obtaining information on the concentration, bioavailability and mobility of REEs in soil and ecosystem quality (Kartal et al., 2006). It gives the digenetic transformation of REEs within the sediment/soils of an ex-mining area and the reactivity of both natural and anthropogenic origin. REEs speciation gives a better understanding of the contamination scenario in sediment/soil.

Bioavailability of REEs was determined in plants. Previously, it has been found that REEs have some positive effects on plant growth (von Tucher and Schmidhalter, 2005). However, little is known about their uptake capacity and the mechanism remains unclear. pH controls mobility and behaviour of REEs in the soil (Violante et al., 2010: Tang and Johannesson, 2010). It puts a significant effect on the complexes, clay content of the soil, lower cation exchange capacity (CEC), redox potential and organic matter due to adhering and chelating nature (Aggelides and Londra, 2000). Such parameters show negative impacts on the bioavailability. However, the mobility of REEs enhanced in the presence of rare earth phosphates (REE-PO_4) and metal hydroxides (von Tucher and Schmidhalter, 2005). Root is the most important part of the plant. REEs promote the growth of the root

system by enhancing the formation of adventitious roots and affecting cell differentiation and root morphogenesis (Zhang et al., 2013).

Inductively coupled plasma mass spectrometry (ICP-MS) is used as a major technique throughout this research. The main reason for the technique's unparalleled growth is its ability to carry out rapid multielement determinations at the ultra-trace level. Even though, it can broadly determine the same suite of elements as other atomic spectroscopic techniques such as flame atomic absorption (FAA), graphite furnace atomic absorption (GFAA), and inductively coupled plasma optical emission spectrometry (ICP-OES), ICP-MS has clear advantages in its multielement characteristics, speed of analysis, detection limits, and isotopic capabilities. It is accomplished by counting the number of ions at a certain mass of the element. A number of different ICP-MS share similar components such as the nebulizer, spray chamber, plasma torch, interface, and detector, but differ significantly in the design of the mass spectrometer and in particular the mass separation device.

1.3 Problem Statement

High levels of REEs in soil, sediments, water, their dispersion in aqueous media and ecological damage are common effects of mining activities all around the world (Gosar, 2004, Horvat et al., 2003, Sajn, 2002, Vreca et al., 2001, Astrom and Nylund, 2000, Durn et al., 1999, Salomons, 1995). Mining activities have been accompanied with many benefits. Apart from these, short comes are more drasting that persist for hundreds of years by leaving a toxic legacy, acid mine drainage and other negative environmental impacts (Hoskin et al., 2000).

China, United States, India, Australia, Brazil, Malaysia, Russia, Egypt, Canada, and South Africa are well known for REEs deposits. Malaysia hosts rare earth minerals, including monazite, xenotime and samarskite from tin ore tailings (Jewell and Kimball,

2014). Transfer of REEs from their point source to the surface of the earth through different pathways is shown in the **Figure 1.1.** Environmental degradation is now a day's closely related to REEs which are related to their mining and processing's (Salomons, 1995).

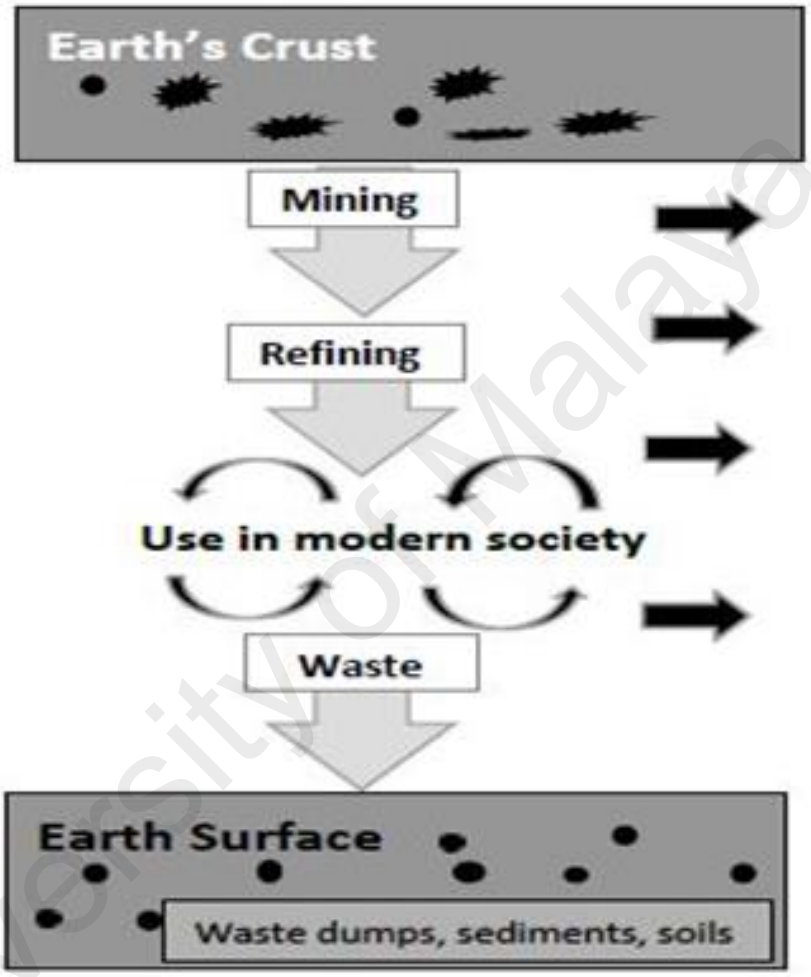


Figure 1.1: Transfer of metals from their mined areas through soil and sediments to the earth crust (Salomons, 1995).

Now the question arises that since the start of mining activities REEs have been exposed to the environment but until now there are few previous studies found on the concentration, speciation and bioavailability. There is a need to detail study REEs in different environmental samples and regions of mining areas. This has become a very interesting issue in recent times.

Mining operations have been carried out in the current study area with many small ponds and big lakes left behind, radioactive waste and mined places which need to rebuild. Due to liability issues existing mining industries are reluctant to explore new resources. To achieve cost effective and long term improvements in mining areas, innovative approaches and technologies need to be adopted and applied. This has drawn much interest to the researchers for the removal of REEs from the environmental components by developing scientifically cost-effective remedial methods and techniques (Aiken et al., 1982). For more than 150 years, mining activities in Malaysia caused tin tailing and REEs disposal waste on large scale (Shamshuddin et al., 1986). There are many problems related to safety and environmental aspects during mine processing and even after its closure.

Rare earths mining and processing activities in Lahat and Kinta valley has created hazardous waste and put harmful impacts on the surrounding environment. So far no study has been done on the speciation and bioavailability of rare earth elements (REEs) in Lahat Perak, Malaysia. Current study focuses more on the chemical form of REEs and their mobility which are more important to control hazards and mitigate harmful impacts on the environment.

1.4 Objectives of the Study

The general objective of the research is to study the impact of REEs in surface water, sediments, soil and plants in the former tin mining catchments of Lahat, Perak and to access the bioavailability of these rare metals in the ecosystem. This work has the following specific research objectives:

1. To determine the concentration of rare earth elements (REEs) in surface water, sediments, soil and plants.

2. To determine the chemical speciation of rare earths in soil and sediments and evaluate their possible risk assessment.

3. To investigate the effects of chemical speciation on the chemical bioavailability of rare earth elements and assess their pollution impacts on the environment.

The main originality of the thesis is to combine, for the first time the geochemical, physico-chemical and analytical techniques to better understand the levels of REEs in the ex-mining area. It is anticipated that the knowledge gained in this study should provide a basis for a possible evaluation of the environmental impacts of tin mining in the Peninsular Malaysia.

1.5 The Scope of Present Study

In the light of all the aspects discussed above about REEs and their effects on environment in Lahat, Kinta valley and surroundings in Perak, Malaysia, it was decided to do present work in ex-mining area. Present study will reveal the facts about the presence and effects of REEs on the environment. Investigations relating to REEs will be done in water, sediment, soil and plants to evaluate their concentration, speciation, bioavailability and potential mobility. Environmental impact assessment will be done in sediment and soil that will be a very useful information in this study area. Main purpose of the study correlates with the hazards of REEs and their presence in environment in abandoned tin-mining land in Malaysia.

1.6 Study Area

Perak is the second largest state in Peninsular Malaysia (Hengky, 2011) with temperature range 23 °C - 33 °C throughout the year, 82.3 % humidity and 312 mm annual rainfall. By its geology largely governed by flanked mountains on the west side with alluvium cover, granitic mountains on eastern side, subordinate schist and low lying land

underlain by limestone hills prominently in the Kinta valley (Khan et al., 2016). Geological, landuse, hydrological and sampling area maps are shown in **Figure 1.2, 1.3. 1.4 & 1.5.**

There is a river flowing along the length of the valley, known as sungai Kinta as shown in **Figure 1.5**. Perak is one of the richest states in the country; richness comes from tin-mining in Kinta district. Bukit Merah, an elongated piece of land is located in Kinta valley, stretching about 1.6 km along the east by Menglembu Lahat, south from Menglembu Township and west by tin mining land. There are many small ponds and a big mining lake in the area.

1.7 Contribution of Dissertation

Rare earth mining process depends on the type of the ore processed during mining and elements which are extracted. In recent year rare earths have been focused much by public inquiry due to natural resource extraction and convergence of environmental narratives. Mining and extraction processes broaden the growth of social movements. In Malaysia, legacy of past projects enhance doubt between community and site developers and highlight strong universal connections and declare environmental inequality of activism around minerals.

In this research, REEs have been studied for the first time on ex-mining land in the state of Perak. Speciation and bioavailability are considered two more important aspects to evaluate REEs in the environment. A new novel, cheap, easy and reliable method has been developed for determining cation exchange capacity (CEC) for the soil. Sequential extraction procedure for chemical speciation has been modified for its simplicity and accuracy. The key findings in this research related to REEs will help to solve environmental issues already undertaken by environmental protection agencies.

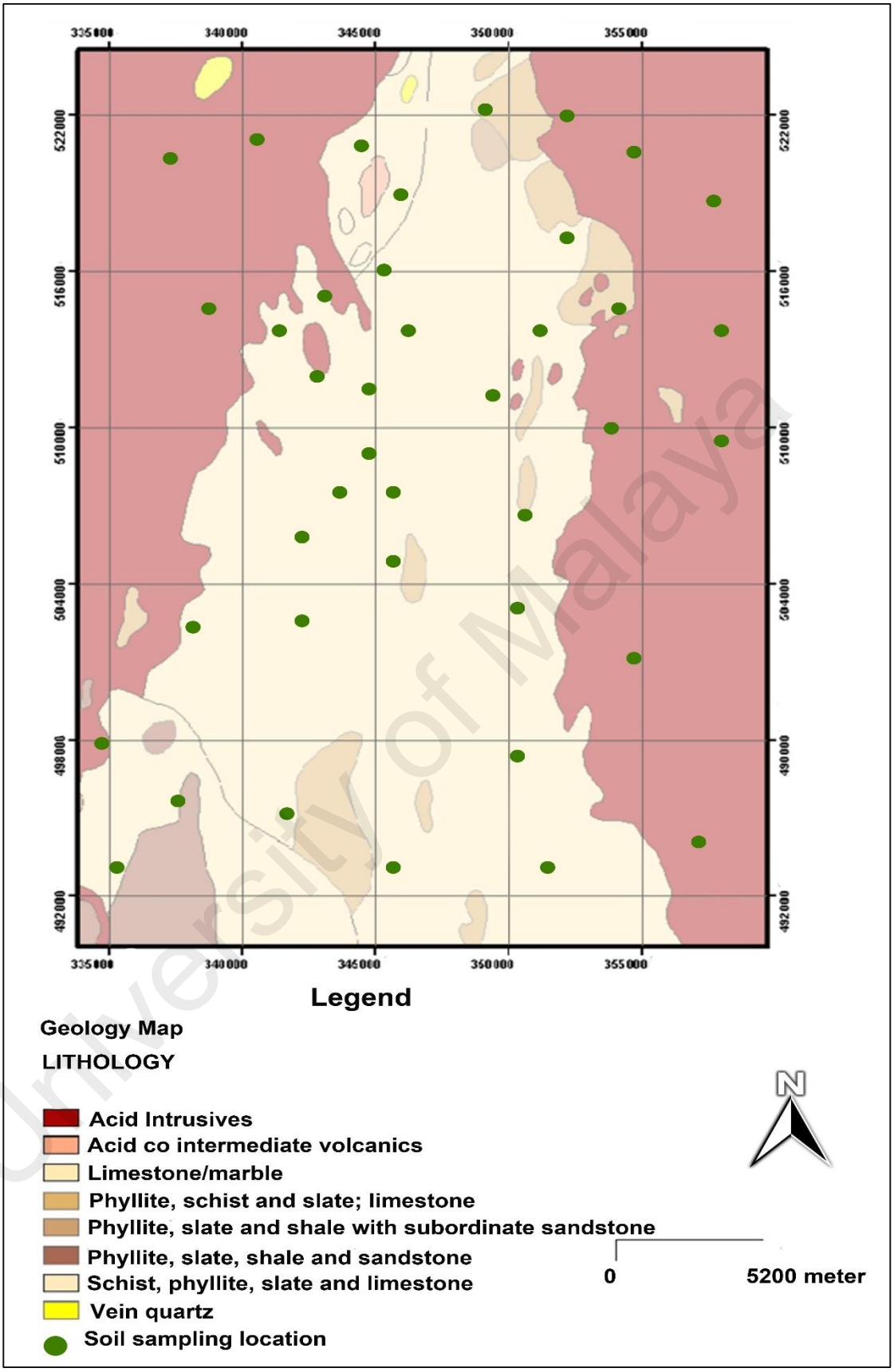


Figure 1.2: Geological map of the Kinta valley, Perak, Malaysia (Modified from Yassin et al., 2015).

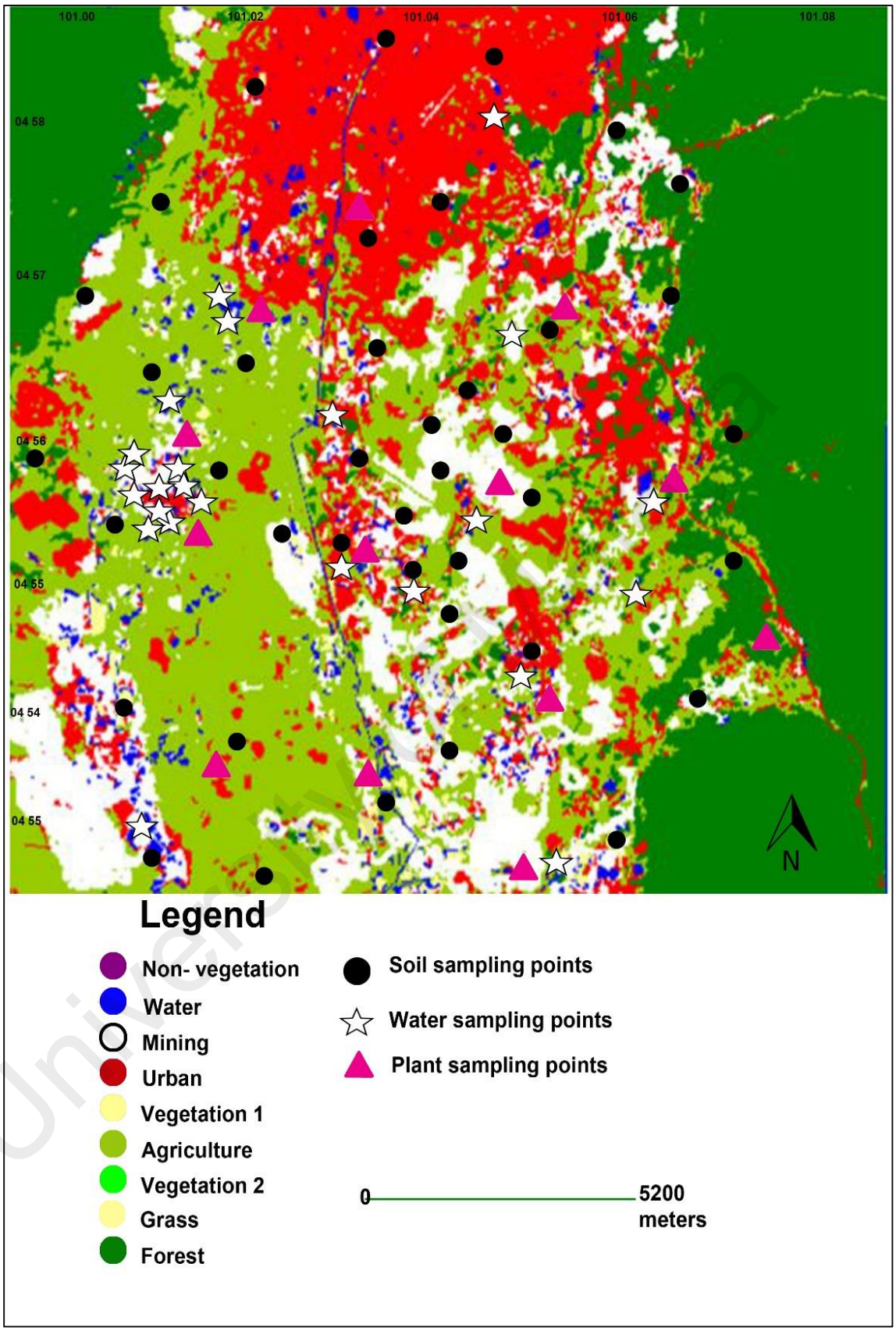


Figure 1.3: Landuse map of Kinta valley, ex-tin mining area in Perak, Malaysia (Modified from Pradhan et al., 2014).

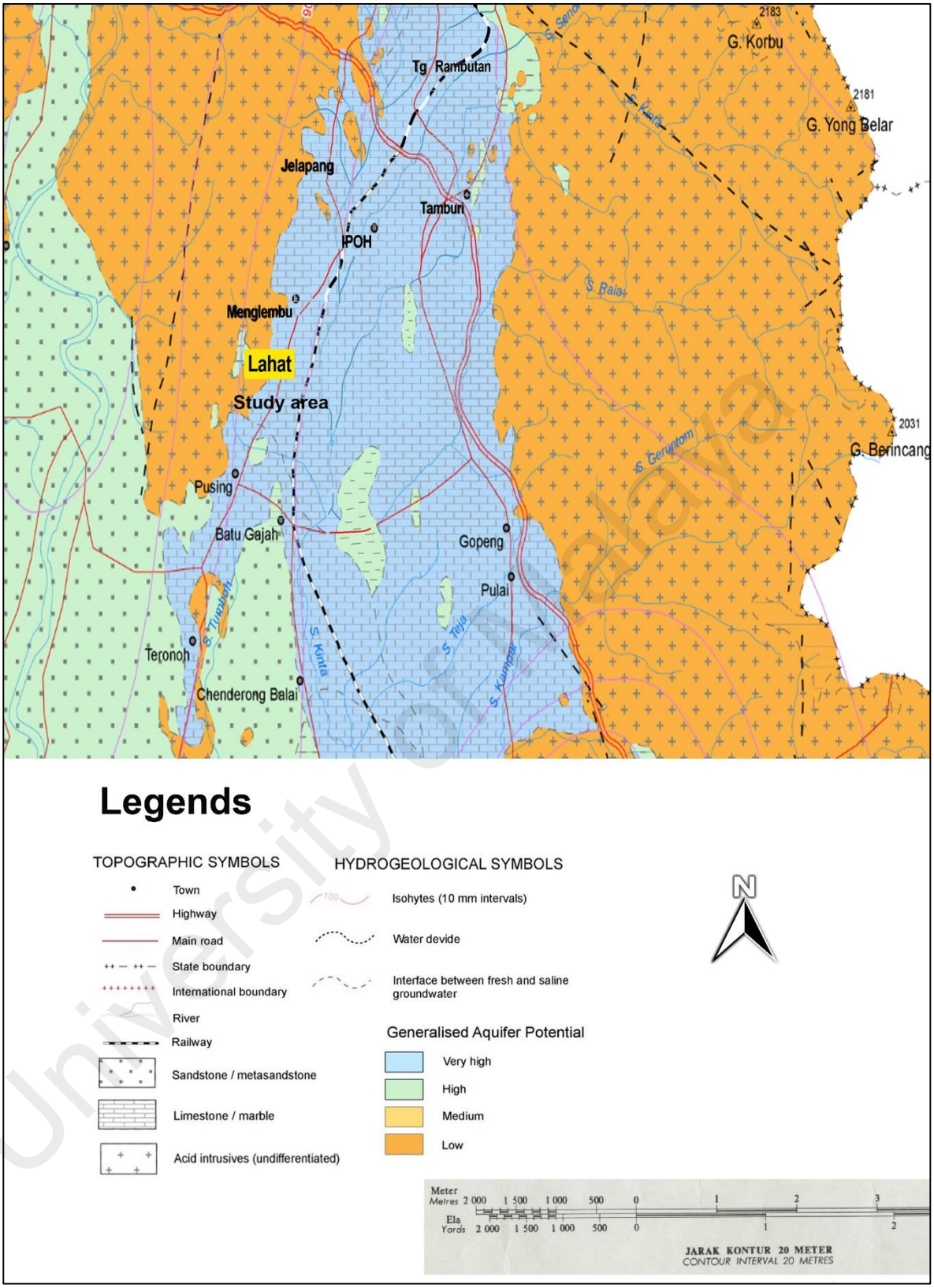


Figure 1.4: Hydrogeology and drainage map of kinta valley, ex-tin mining area in Perak, Malaysia (Mineral and Geoscience department, Perak. 2008)

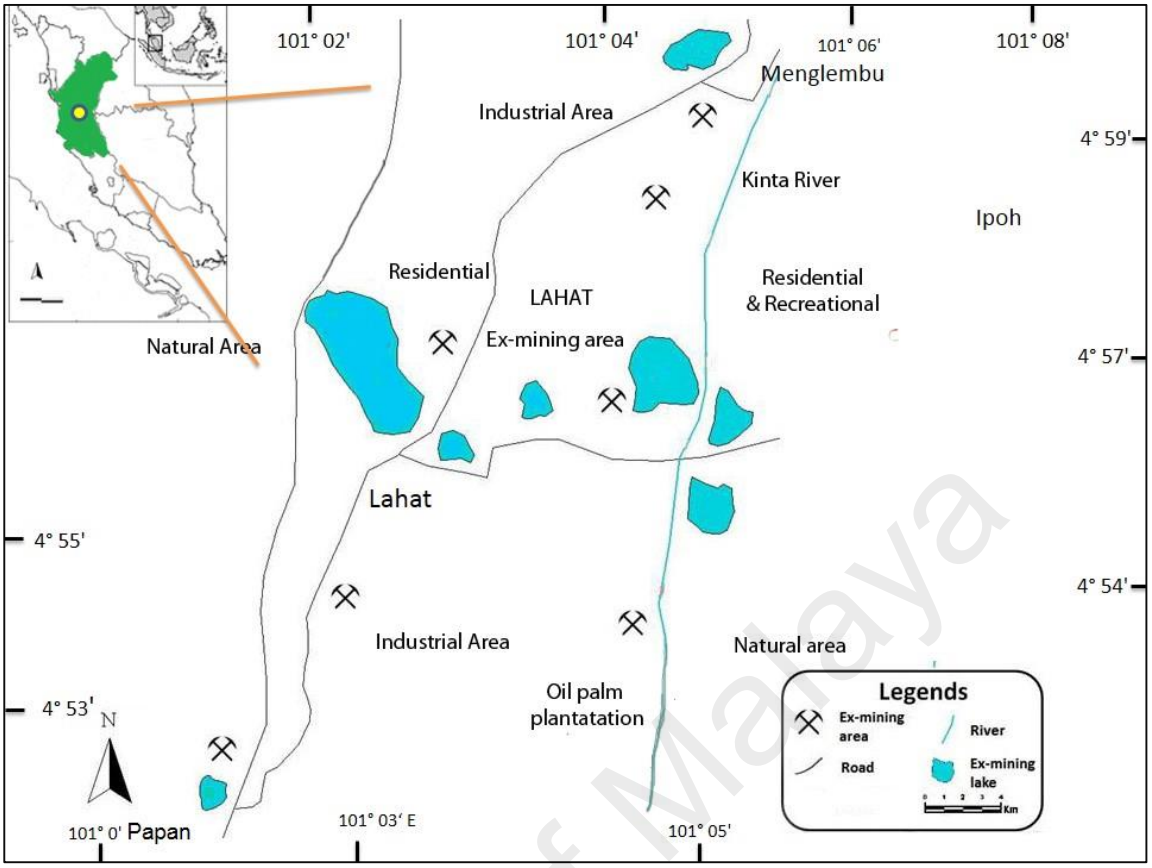


Figure 1.5: Map showing the current study area.

1.8 Thesis Outline

The thesis entitled "Speciation and Bioavailability of Rare Earth Elements (REEs) in ex-tin mining Area: A Case Study from Lahat, Perak, Malaysia" is divided into six chapters.

Chapter 1: Introduction

This chapter describes the general background of Rare earth elements (REEs), speciation and bioavailability that have been the main objective of this study. Study area has been discussed. Scope of the current research and its contribution have been significantly described.

Chapter 2: Literature Review

This chapter comprises of a detailed studies of REEs, their characteristics, importance, global production, applications and determining techniques. REEs have been discussed for their environmental impacts related to speciation, bioavailability in different environmental samples and as pollutants.

Chapter 3: Methodology

The materials used and method adopted for the determination of REEs concentration, speciation and bioavailability have been described. Also include discussion on statistical methods used for analyzing the data obtained from physical and chemical parameters.

Chapter 4: Concentration of water, sediment and soil

This chapter elaborate the results and discussion related to the concentration and physical parameters of REEs in water, sediments and soil.

Chapter 5: Speciation study of sediments and soil

This chapter describes the detailed results and discussion of speciation study of sediments and soil based on sequential extraction procedures. Potential mobility based on speciation has been calculated and described.

Chapter 6: Plant analysis for REEs bioavailabilitiy

Bioavailability of REEs found specifically in plants in their different parts has been discussed in this chapter.

Chapter 7: Conclusion

Summarized part of the research has been given in this chapter.

CHAPTER 2: LITERATURE REVIEW

Following chapter provides background information about the present study and limitations of previous work. It describes the methodology used by the scientists, health risks, environmental and economic impacts of earlier studies. To investigate any issue or to proceed chemical analysis, analytical instruments and measurements play a key role. Some utilized for metals, non-metals, trace elements, ionic liquid crystals, nanomaterial's while other relates to the geology of earth science, their minerals, sample detection, concentration and to save natural environment for the betterment of human beings.

2.1 Introduction to rare earth elements (REEs)

Lanthanides are 15 elements termed as rare earth elements (REEs) (Wall, 2014). These include lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu). Scandium (Sc) and Yttrium (Y) due to similar physicochemical behavior also include in Lanthanides. Important and commonly occurring REEs are shown in **Figure 2.1.**

Figure 2.1: Some important rare earth elements (REEs) (Van Gosen et al., 2014).

REEs are known as critical elements because of high tech industrial applications (Charalampides & Vatalis, 2015, Taylor & McClennan, 1985). REEs are categorized as light rare earth elements (LREEs) from La to Gd including Sc, also known as cerium group and heavy rare earth elements (HREEs) from Tb to Lu including Y, also known as Yttrium group as shown in **Figure 2.2**. After heavy metals abundance such as lead, molybdenum and arsenic in earth crust, two important rare elements (Ce and Y) are also present in higher concentrations. La and Nd have same occurrence as lead and thulium but more than gold, platinum and iodine (Reiners, 2001, Richter et al., 2006).

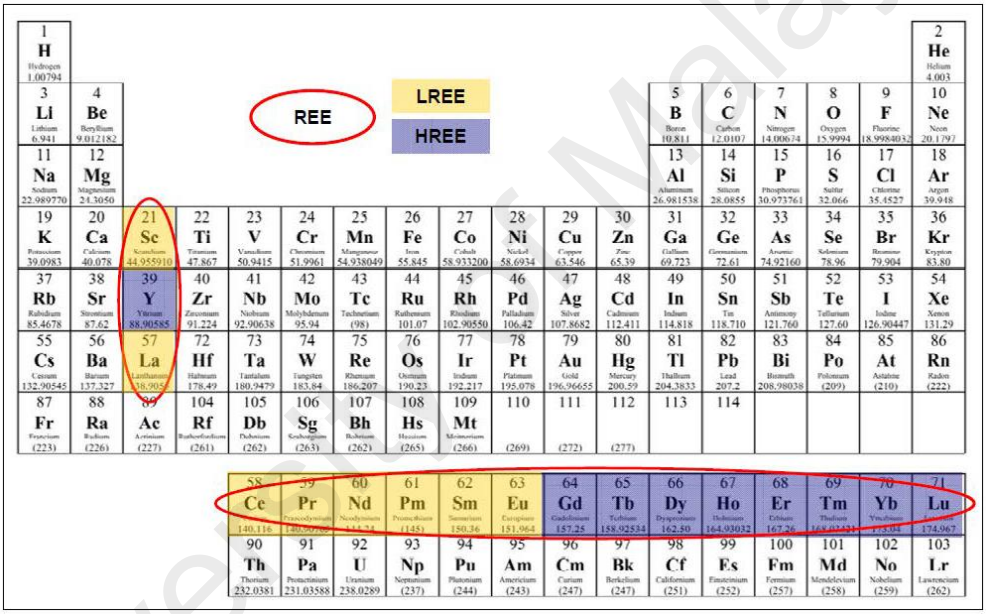


Figure 2.2: Periodic table of the elements showing the division between LREEs and HREEs (Schüler et al., 2011).

2.2 Sources of rare earth elements (REEs)

REEs are not rare in nature but extracted as a byproduct during mining of other elements or metals (Oko-Institut, 2011). First REEs was discovered in 19th century, cerium being more abundant was found in high percentage. REEs mostly occur in earth's crust and show great diversity in geological deposits.

Major ore deposits of rare earths include monazite, bastanasite and xenotime. Monazite (Cerium phosphate) with monoclinic unit contains LREEs like Ce, La and HREEs like Nd in greater amounts, found mostly in acidic igneous rocks, metamorphic rocks, vein deposits, placer deposits as host rocks eroded and resistant to weathering, minerals crystallized under low temperature and pressure. Xenotime (Y-phosphate) with tetragonal geometry contains HREEs along with uranium and thorium, crystallizes under high temperature and pressures, primarily called Yttrium phosphates mineral and is a constituent of granitic and gneissic rocks. Igneous rocks contains 100 ppm of lanthanides in their minerals where in sedimentary rocks such as carbonates and sand stones (high conc. of REE and Y), clay minerals are in abundance. LREEs strongly concentrate in continental crust due to large radii and less compatibility with other minerals. 80-90 % of REE deposits contain La, Ce, Pr, and Nd.

Among metamorphic rock minerals, efficient amount of REEs are found in garnet, fractionating the heavier lanthanides. Association of radioactive elements like U and Th with REEs pose environmental issues (Vaca-escobar and Villalobos, 2010). During 1950's and 1960's, marine and alluvial placer deposits considered most important source of REEs. Thorium by weight is present in monazite formed in granitic rocks. Metallothermic and electrolytic methods are considered more successful in rare earths production (Gupta & Krishnamurthy, 2005).

2.3 Characteristics of rare earth elements (REEs)

Unique chemical properties of REEs urged scientist to find application in geochemical studies and planetary systems (Bwire et al., 2003). All REEs occur in trivalent state except Ce^{4+} and Eu^{2+}. One of the basic property of REEs is Lanthanide contraction, due to decrease in ionic radii from La^{3+} to Lu^{3+} by progressive filling of electrons in inner shielded 4f-orbital. This property leads REEs in studying fundamental processes

governing oceanic cycling. REEs have been utilized to understand geo-chemical exchange between crust and ocean (Elderfield et al., 1988).

Most of the REE compounds are phosphatic. Naturally lanthanum exists as silicates, carbonates, oxides, phosphates and ion-halogenated compounds in minerals. REEs never occur as individuals so said that: nature no better than chemists in separating them. Weathering process causes fractionation of REEs (Tyler, 2004). According to Oddo-Harkins rule, elements with even atomic number are more abundant than odd atomic numbers however quantity decreases with increase in atomic number (Pendias and Pendias, 2001, Wen et al., 2001). Word rare, refer to the separation of rare earth elements (REEs) from other elements and earth refer to the old term for oxides as REEs were first identified as rare earth oxides (REO) (Richter et al., 2006). Magnetic and spectroscopic properties depend upon bindings. Rare earth compounds are predominantly ionic in nature, do not exhibit as covalent bonding or crystal field stabilization and show high affinity to compounds containing strong ligands (F^-, OH^-, O^{3-}) (Bulman, 2003). REEs show some bonding with co-ordination compounds. Sc and Y forms two series of transition elements with La and actinium (Ac). Closely related chemical properties of REEs constitute their behavior in natural environment (Harbon, 2002).

REEs are generally lustrous from grey to silver in colour, soft, malleable, ductile, reactive, strongly paramagnetic with strong anisotropy and difficult to separate with high electrical conductivity and trivalent charge occur as monazite (Raileanu et al., 2013). REEs show similarity with Al and low solid solubility forming intermetallic bonds with alloying elements resulting in decrease electrical conductivity without affecting ductility (Pai et al., 1995, Handbook, 1979). Lanthanides with lower atomic number find more common and more abundant ores than high atomic numbers. Gadolinium and Dysprosium classified as medium weight lanthanides. In July 2011, mining of REEs resumed at

Mountain pass and started at mount weld reached at full production level in 2012 supplying globally 40,000 tons/annum (Protano and Riccobono, 2002).

REEs occur in dispersed form. Cerium being 25th most abundant element. Few exploitable deposits are known as rare earth minerals. REEs are known to be found in more than 200 minerals. Many REEs are associated from the source from which they have been derived. Elemental forms of REEs derived from their ores are soft, malleable, ductile, magnetic, reactive, optical assets with lustrous surfaces (Merten and Buchel, 2004). Increase in melting points from cerium (798 °C) to leutetium (1663 °C) have been observed. Except scandium, yttrium, lanthanum, ytterbium and leutetium, REEs show paramagnetic and strongly magnetic anisotropy. In aquatic ecosystems REEs are in trivalent state (Ln^{3+}) except cerium (Ce^{4+}) and europium (Eu^{2+}) (Merten & Buchel, 2004, Gupta & Krishnamurthy, 2005, Gupta & Krishnamurthy, 2004). Average abundance of REEs in earth crust vary from 66 μg g^{-1} to 0.5 μg g^{-1} (Greenwood and Earnshaw, 1984).

2.4 Mineralogy of rare earth elements (REEs)

REEs naturally occur in a diversity of mineral types. HREEs and Y are mostly associated with minerals such as xenotime, euxenite, yttrotantalite, samarskite, and gadolinite while LREEs are found in monazite, bastnasite, ancylite, lanthanite, stillwellite, allanite, cerianite, britholite, and loparite (Chakhmouradian & Wall, 2012). Bastnasite, monazite and xenotime ores are mostly extracted around the world in commercially operating mines. High concentration of REEs produces its own minerals. Despite of more than 200 REE minerals, only three ores considered suitable for extraction: Bastnasite, xenotine and monazite (Gupta & Krishnamurthy, 2004, Weng et al., 2013). **Bastnasite**, a carbonate mineral [(Ce, La, Y)CO_3F] found associated with hydroxyl-bastnasite [(Ce, La)CO_3(OH,F)], having dull to lustrous form and occur in different colors varying from white, gray, tan, brown to yellow or pink. This mineral was found similar to parisite [Ca

(Ce, La)$_2$(CO$_3$)$_3$F$_2$] and in vein deposits, pegmatite's and contact metamorphosis zones. It is highly enriched in LREEs such as cerium, lanthanum and yttrium (Haque et al., 2014, Keith et al., 2010). **Xenotime** and **monazite**, two phosphate minerals, found together, crystallize under different temperature and pressure regimes containing any of HREEs or LREEs. **Monazite,** an enriched LREE and phosphate mineral bearing thorium [(Ce, La, Y, Th)PO$_4$], characterized by low crystallization temperature and pressure with 60–62 % RE oxides, commonly present in yellow to brown or orange brown crystals having transparent and viscous shiny surfaces. Thorium imparts radioactive properties and waste produced from such mineral need special disposal methods, accounts disorder for financial extraction. Generally, minerals with radioactive properties are not easy to handle and process (Keith et al., 2010, Sprecher et al., 2014). **Xenotime**, an yttrium phosphate mineral (YPO$_4$) crystallizes under high temperature and pressure with enriched HREEs and minor component of granitic and gneissic rocks. In nature this mineral found as a part of acidic and alkaline rocks with lustrous surface and yellow to reddish brown in color (Keith et al., 2010, Harbon, 2002, Melfos & Voudouris, 2012).

Uranium ores have also been found to contain REEs in appreciable amounts. Processing of such radioactive minerals for REEs is very challenging to the world's producer and supplier countries. Four countries; China, USA, Australia and Malaysia are well known for REEs deposits. China has bastnasite and xenotime deposits while USA principally contains bastnasite deposits. Australia has major RE bearing minerals such as monazite and xenotime whereas Malaysia is known for xenotime deposits only (**Figure 2.3)** (Australia, 2013, Haxel et al., 2014).

2.5 Distribution of rare earth elements (REEs)

Rare earth distribution in minerals debated high co-ordination numbers (10-12) are Cs selection, with low co-ordination numbers (6) are Y selection and with intermediate

numbers (7-9) have complex composition for both LREE and HREEs. Availability and distribution of REEs identified by factors such as ionic radius, appropriate bonding forces, charge and optimum ionic radius. Similar ionic radii and oxidation states place REEs as substituent in crystal structures. High concentration of REEs is required for forming their own pure minerals. REEs enriched environment is divided into two categories i-e igneous and hydrothermal processes called primary deposits while weathering and sedimentary processes called secondary deposits. These two classes further subdivided on the basis of their occurrence, mineralogy and genetic associations. Orris and Grauch, 2002 gave most comprehensive list of REEs deposits and occurrence (Orris & Grauch, 2002). REEs distribution in different deposits is shown in **Figure 2.3**.

The distribution of this group of REEs shows significant differences in their contents in automorphic and alluvial soils in areas with different geological bases. It also indicate that the lanthanum contents vary in the range of 1.6–42 mg kg^{-1} in the Kamenica–Zletovska Rivers quarter terraces. Lanthanum distribution is specifically correlated with the older volcanic formations of Paleogene flysch (with a median of 15 mg kg^{-1}). Cerium contents vary from 3.6 to 65 mg kg^{-1} in the topsoil sample, with no significant variations between the contents in the topsoil versus the subsoil layer. The HREEs are deposited as geochemical association predominantly automorphic soil types on the terraces in the Bregalnica basin (Rollinson, 2014, Balabanova et al., 2013, Balabanova et al., 2015).

2.6 Rare earth elements (REEs) global production, supply and demand

USGS reported total worlds RE oxide reserves 99 million tons (MCS, USGS 2010). Actively mining RE countries includes China, India, Brazil, Malaysia, and USA as shown in Figure 2.4. Total worlds REE resources up till 2012 are 114 million metric tons with 48.3 % worlds reserve dominates in China, 16.7 % by common wealth of independent states (CIS) and 2.7 % by India.

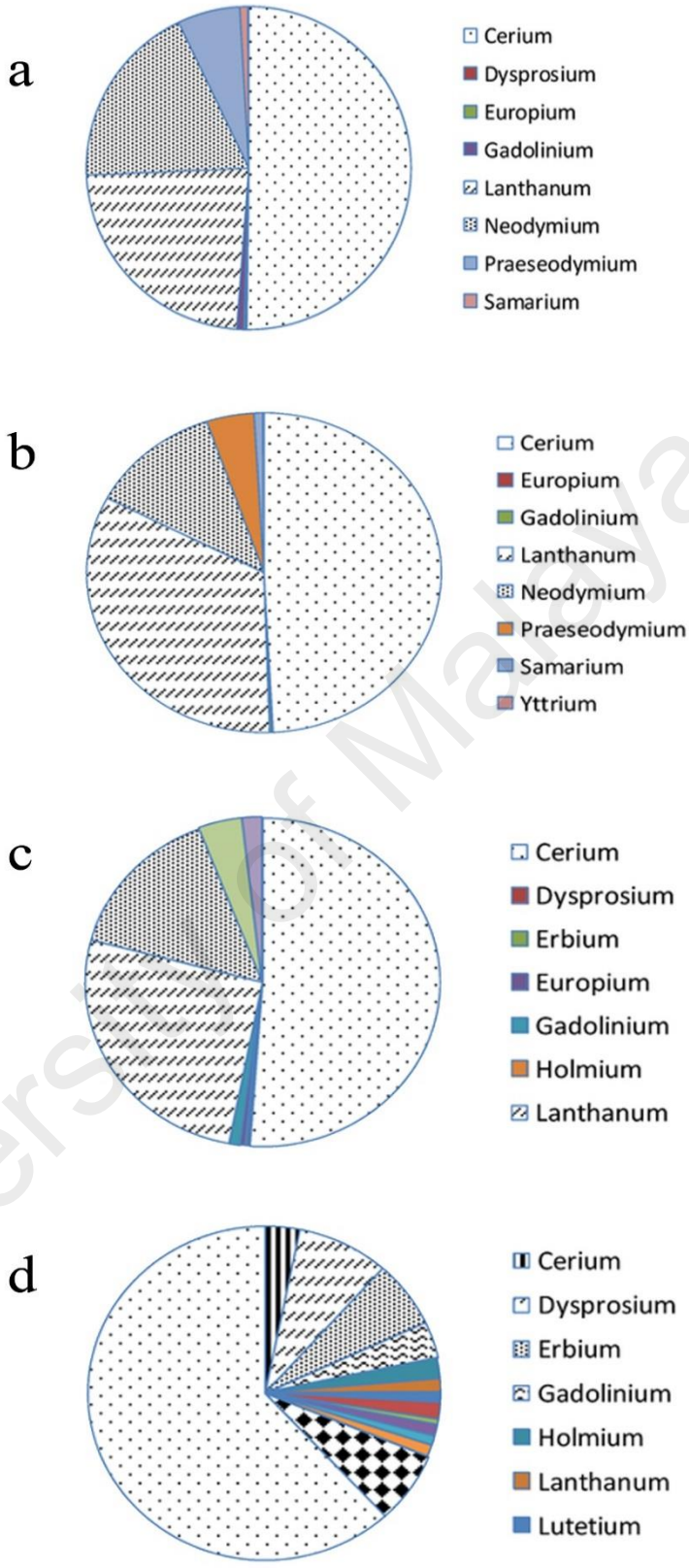


Figure 2.3: Rare earth elements distribution in (a) Bayan Obo, China (b) Mountain Pass, USA; (c) Mount Weld, Australia; (d) Lahat, Malaysia (USGS, 2013: Haque et al., 2014).

Global REE demand continues to grow until 2016. Rare earth importers are Japan, Germany, France and USA. Largest importer in 2008 was Japan and USA followed by Germany, France and Australia. China export 48,000 tons of REEs in 2008 while Australian based companies export products like alloys, industrial metals misch metals, 15 cerium compounds and solutions, oxides of all REEs, ferrocesium and lighter flint alloys. China started REE supply in 1980's and in 1990's become principal supplier (Rose, 1960).

In 2008 Japan stands 3rd largest exporter of REEs after many European and Middle East countries. USGS reported large undiscovered reserves in the world to meet global demand as well as local Chinas demand as shown in **Figure 2.5.** REEs global production increased up to 123,000 tons in 2009. Increasing demand of REEs corresponds to their use in low C technologies. Most countries put emphasis on achieving global diverse supply; improve recycling and resources, reuses and identifying substitutes. Orthophosphates of LREE or Cerium group called Monazite, flurocarbonates as Bastanasite while orthophosphates of HREE or Y group called Xenotime. Of these deposits 80 % holds China, 11 % USA and 5 % India (Meyers, 2002). REEs exist in carbonate complexes [$Ln(CO_3)_2$] and 99 % in alkaline lake water. LREEs form strong complexes than HREEs. REEs considered providing valuable tracers or signature information (Johannesson et al., 1995).

REEs are not rare in nature but their extraction for promoting concentrations to appropriate level is very challenging (Report, Nolans project 2012).

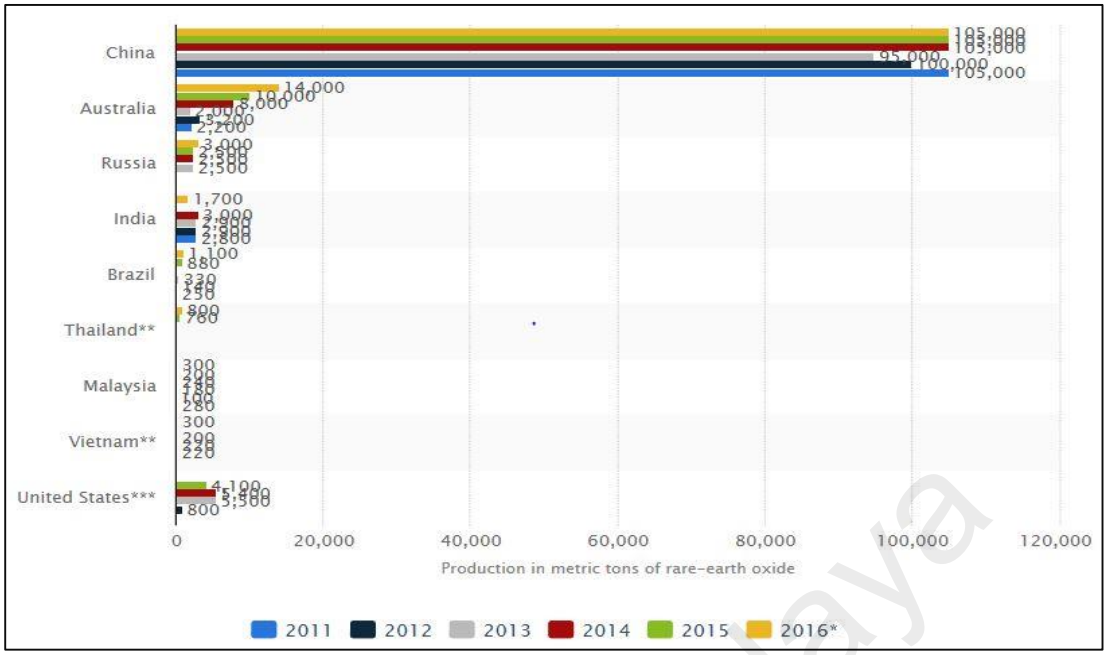


Figure 2.4: Top countries in rare earth mine production worldwide during 2010-2013 (USGS, 2014).

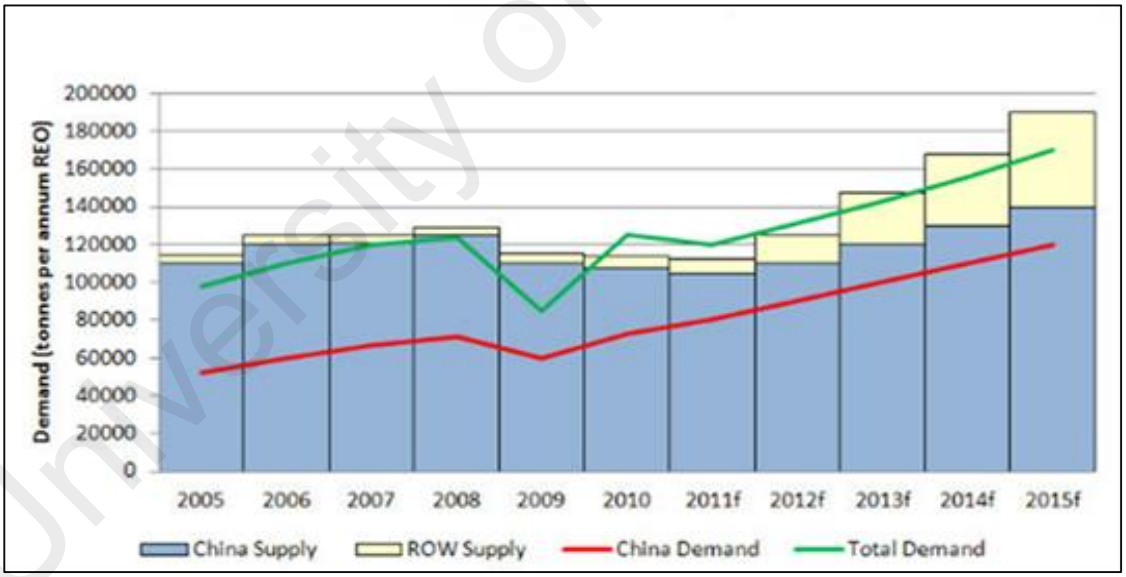


Figure 2.5: Rare earth supply and demand from 2005-2015 (USGS, 2014).

2.7 Applications of rare earth elements (REEs)

REEs being major component of advanced material in high tech and green energy sector referred as ″Seeds of technology″ where durability, low carbon emission and robust performance required. In most countries of the world, commercially used REEs constitute technical applications. In 1903, industrial process and commercial utilization of REEs started after discovering their pyrophoric properties and alloys for flint and incandescent mantle containing thorium. In 1907, ferrocesium lighter flint discovered as first industrial product and others REEs in all countries especially United States (Calvert, 2005).

In nuclear technology REEs are useful as neutrons absorber to nuclear reactors and in neutron shielding metals. REEs show ease of oxidation, applied as reducing agent for other metals, as getters and for improving the physical properties of alloys. Carbon and other impurities removal from cast iron, grain refining in high grade steel, aluminium and magnesium containing alloys, rolling, tensile strength, creep, corrosion resistance properties in Cr, improved by REEs. REEs used as catalyst, permanent magnets, fluorescent, pigments, miscellaneous (superconductors, data saver, laser material, cement additives, glass fiber cables, magnetic cooling, grease, jewellery, solar energy system, textile, medical techniques) constitutes economic importance (Osoon, 2005). Lighter flints containing Auer incandescent mantles comprise classical applications.

Misch metals used in Ni metal hydride, rechargeable batteries like laptops, computers and mobile phones depends on their ability to absorb and store hydrogen in smaller space. REEs show applications as fuel cells, fluid catalyst; in cracking process as zeolites catalyst cracking efficiency enhanced 1-5 % of RE chlorides, hydrocarbon oxidation as cerium oxide used in self-cleaning ovens, autocatalytic counter and CFC catalyst (Darcy et al., 2014). REEs used as major components of solid state lasers, europium in addition to glue of postage stamps read by electronic sorting machines. Promethium serves as heat source

in space crafts, satellites, space probes and nuclear powered batteries (Bergmann, 2005). High performance permanent magnets are usually based on REEs properties such as optimal, magnetic and alloy. Holmium and dysprosium used as pole pieces for high field and low temperature magnets. Permanent magnets used in computers, electrical, mechanical and automotive engineering, navigation, telecommunication, aviation and space operation.

Combination of REEs with transition metals acts as powerful permanent magnetic material. In glass industry REEs are used for colouring and decolouring as lanthanum used in high quality lenses, scientific instruments and cameras. REEs find use in goggles for welders and glass workers, electronic applications in band lamps, microwave filters (Sm), cathode ray tubes (CRT), ceramic for electronics (La, Ce, Pr) and flat plasma TV screens (Eu, Tm, Y, Pr) (Krebs, 1998, Bergmann, 2005). REEs being important laser materials used in laser medicine technology for therapeutic purposes, surgical procedures, dentistry, dermatology, angioplasty, ophthalmology, urology, neurosurgery and gastroenterology. Papillomavirus lesions treated by Neodymium YAG lasers (neodymium-doped yttrium aluminium garnet; Nd:$Y_3Al_5O_{12}$) and lithotripsy by holmium YAG lasers.

REEs perform anticoagulant, antimicrobial, cytotoxic, and phosphate binding with maximum effect on Ca^{2+} depending processes, anticancer diagnostic purpose and therapy (Zaak et al., 2003, Shamamian & Grasso, 2004). Medical uses of REE began with antiemetic containing cerium oxide for the treatment of vomiting, gastrointestinal disturbances, neurological disorders and cough. Hyperphosphatemia, disease developed by chronic renal failure need to lower phosphate levels. Lanthanum carbonate, RE salt due to less toxicity and low intestinal absorption capacity show highly effective phosphate binding properties (Harrison & Scott, 2004, Hutchison & Albaaj, 2005).

Most important use of rare earths lies in the magnets (Hollins, 2010). Neodymium-iron-borates magnets and smarium-cobalt magnets considered largest and strongest permanent materials. Neodymium magnets being hardest used in Hard disk drives (HDD), biggest application of recent era and in speakers, wind turbines, luminescence and hybrid electric motors etc. Worlds per year RE oxides consumption estimated 765, 000 tons. RE phosphorous used in X-ray photography, fluorescent lights, computer monitors, colour TV screens, trichromatic and super deluxe lamps. In industrial robots, space technology and military plans permanent magnets used in limiting motors (Cannon, 1980). Neodymium-iron-boron (Nd_2-Fe_{14}-B) permanent magnets constitute over 25 % of worldwide market in high tech (Davies, 1986). One of men's greatest achievements lies in the discovery, exploration and utilization of nuclear fission processes. REEs show more affinity towards nuclear technology with high capture cross-section for thermal neutrons and same time acts as poison for nuclear fuel if present in high concentration.

2.8 Determination techniques for rare earth elements (REEs)

REEs are determined at ppm level in uranium, expressing difficult task (Ahmad et al., 1984). Solvent extraction, distillation, precipitation followed by atomic absorption spectroscopy (AAS), X-Ray fluorescence (XRF), DC-arc emission spectrometry and Inductively coupled plasma atomic emission spectrometry (ICP-AES) are some of the techniques used to determine REEs in different samples but these instruments lack reliability and sensitivity. Neutron Activation Analysis (NAA) and Inductively Coupled Plasma Mass Spectrometry (ICP-MS) for REEs detection proves quite sensitive techniques. Main attraction to analytical chemists with broad variety for REEs lies in solvent extraction not only because of time savings but gives resolution and reproducibility in results. Geochemical reactions at low temperatures fractionate the REEs in water and sediments (Johan et al., 2000). Now a days, NAA and ICP-MS techniques are usually applied to determine REEs in soil, sediment and water. Until 1950s,

for REEs separation, fractional crystallization and precipitation superceded by ion exchange and solvent extraction considered laborious and inefficient techniques (Gupta & Krishnamurthy, 2005).

Inductively Coupled Plasma Mass Spectrometry (ICP-MS) technique was first designed in 1980s (Dai et al., 2014) and used as a versatile detection technique for trace and rare elements. ICP-MS (Agilent 7500) is applied to trace and ultra-trace measurement of >70 elements from <1 ppt to >500 ppm (9 orders linear range). Spectral simplicity shows that every element (except In) has an isotope which is free from direct overlap. Speed of multi-element analysis lies for typical multi-element acquisition in 1-2 min (~4 min including rinse). Flexibility to optimize for specific applications such as automated set-up and auto tuning give improved ease of use. Fast semi-quantitative analysis give accurate data without calibration and measurement is based on comparison of relative isotope sensitivity. Detection limits are 10-100 times superior to those of ICP-AES and ICP-OES. It requires small amount of sample and has excellent dynamic range.

2.9 Environmental impacts assessment of REEs (as pollutants)

Risk and impacts of REEs availability depends upon life cycle costs and geopolitical considerations suggesting risk to increase in next few decades with supply disruption in the products sustained heat are anticipated. This is a critical issue not a crisis. Mining and processing techniques of REEs show considerable variations due to their diversity in deposits. Surface mining, one of the methods of rare earth extraction, performed separately or in combination with underground mining. Mining methods for placer deposits of REEs depend upon physical condition whether submerged or on land. REEs hardly mined separately. Mount pass in California operated exclusively only for REEs recovery while in China extraction from Bayon Oboyo REEs extracted as a by-product with 99.9 % purity (Zhondge, 2009). Oxidation and reduction can be useful in separation

processes for REEs, with fractional precipitation, crystallization, solvent extraction and ion-exchange, all differing in their basicity.

Anthropogenic sources considered main source of environmental pollution for REEs. Majority of REEs pollutants come from industrial effluents. Presence of REEs in aqueous media and atmosphere occur due to extraction from ores and refining by ion-exchange chromatography. REEs in the atmosphere are caused by oil based power plants and automobiles exhaust effecting not only air but also plants. REEs used as fertilizers by Chinese for more than 20 years (Zhang et al., 2001), now frequently applied in agriculture, entering in environment disturbing biogeochemical cycles of REEs causing adverse effects on air, soil and water, finally enters into human beings through food path. Therefore in most countries REEs restricted for only use in industries (Ichihashi et al., 1992).

Liming increases the pH with decrease in REEs concentration. High concentration of REEs up to 30-40 µg L^{-1} also determined. Soil loading capacity of REEs after emitting from agriculture and industry through mining, sewage, sludge and factory effluents increased (Jones, 1997). Generally REEs prove to be hazardous and fatal for health and put negative impacts. In extracted soil, REEs found in water soluble fractions, carbonate bond fractions, sulphide bond fractions, exchangeable fractions, organics and residual fractions. Potentiometric calculations are negatively affected by high amounts of REEs in different environmental samples (Shan et al., 2003). Transformation and distribution of REEs depends largely on Physico-chemical properties of soil. Acidity of soil causes leaching of REEs (Pang et al., 2002). Alkalinity show negative correlation with uptake of lanthanides indicating increased complexation with reduced bioavailability. In sea water depletion of REEs into LREEs and HREEs occur due to complexation with important ligands. REEs mining and processing proves a dirty business, economically

rebuilding the supply chain, domestically are prohibitive and environmentally unacceptable. Aggressive R & D agenda is recommended for REEs alternatives, new applications, REE free technology, recycling, and process optimization.

Recently, many environmental issues are concerned in REE mining and processing due to lack of environmental regulations and control over like xonetime in Malaysia placer deposits contain 2 % Uranium and 0.7 % Thorium, main cause to fail industrial plant in area (Yusoff & Latifah, 2002). Similarly beach sand processing banned due to environmental concerns in China, Australia and Europe. Chemicals used in processing of REEs proved hazardous likewise in China causing diseases to local irritants, destruction of farms and water pollution (Hilsum, 2009). To control environmental issues China stopped rare earth production facilities that impacts on global supply. World's largest institute for REEs, the Batou industrial institute, working with seven projects for technology refining and saving the environment (Daily, 2010).

Recycling of REEs has been a difficult and expensive process. Neodymium can be recovered from Nd-Fe-B magnets that produced large amount of Nd scraps (Binnemans, 2013) and recovery of rare earths is a major problem today in the world due to high cost, low yield recycling processes, not feasible commercially. However, the most promising technology used by Japan, the only country in the world is metal liquid extraction with 1 % recycling capacity (EPOW, 2011). Electric transactions, motors, regenerating braking systems of each hybrid vehicles and batteries contain about 20 kg of REEs. LCD and plasma also contain REEs due to spectroscopic properties. Tb^{3+} show green fluorescence and Eu^{3+} show red with high thermal stability.

According to EPA, REEs processing waste dumped in stream water possess hazardous potential, classified as waste solvent due to ignitability, zinc waste mercury contaminated, spent lead filter cake due to toxicity and solvent extraction (Eliseeva & Bunzli, 2011).

During mining and processing of REEs, major environmental risk are related to waste water, process chemicals and high surface area particles. REE affected areas, if not properly managed and controlled when exposed to weathering, contaminate air, soil and water. The solid, radionuclides, radons, ore-bearing heavy metals, sulphates and organics in trace amount acts as pollutants in areas affected with REEs. Fugitive dust contaminates air and soil in the surroundings. Precipitate events and dam overtopping transfers the pollutants from catchment to surroundings soil and surface water bodies through surface runoff water.

A serious long term environmental damage occurred when dam fails due to poor construction or from catastrophic events, termed as worst case scenario. Poor operation, design, handling, management of REE mine and concerned pollution control system collectively reduce the risk of REE environmental contamination due to REE mining and processing activities as described in **Figure 2.6**.

Environmental components of REEs sustainability have been emphasized in all aspects whether positive or negative (Yang et al., 2013, Ichihara & Harding, 1995). However, difficult to trace environmental aspects of REE compared to heavy metals. Leaching has been an issue of interest in Chinese environmental degradation (Cui et al., 2009). Some industrial, hazardous waste, when disposed of causes unrecovered REEs. China as high in REEs production causes serious environmental damage in areas with mining and processing, if in agreement with limited environmental regulations.

Bayan Obo mine, after 40 years of operation, radioactively contaminate soil, water and vegetation. Chinese society of RE stated, every tons of REE produced, generate 8.5 kg of fluorine and 13 kg of dust along with 9,600 - 12000 m^3 of waste gases with dust concentrate, SO_2, 75 m^3 acidic waste water, HF and 1 ton of radioactive waste residue. Sponification process produces harmful waste water. By estimation, up till 2005, process

generates 20-25000 tons of waste water and 300-5000 mg L^{-1} total ammonia nitrogen concentration (Eliseeva & Bunzli, 2011).

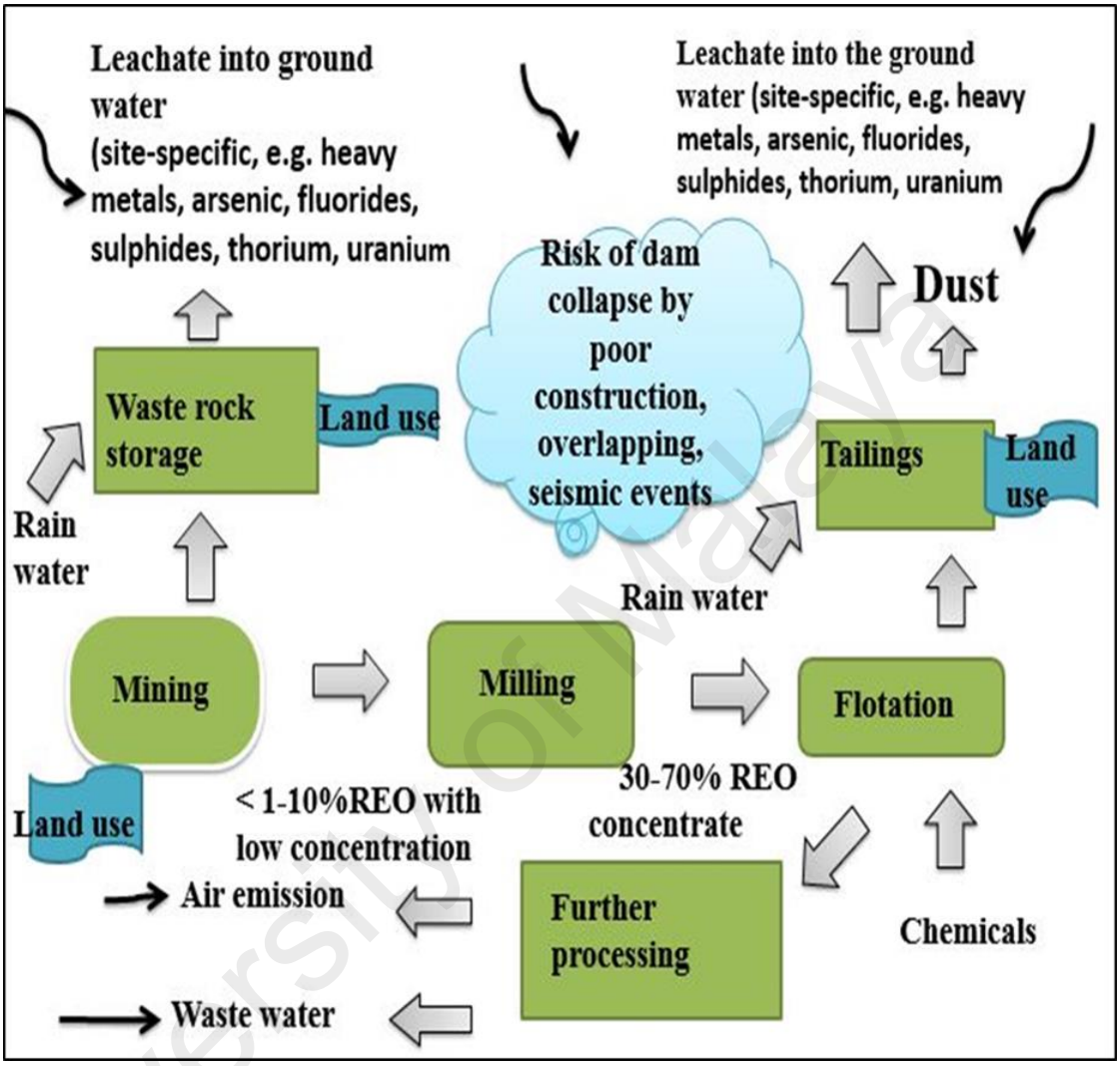


Figure 2.6: Risks of REEs mining without or with insufficient environmental protection systems (Schuler et al., 2011).

Radioactive elements like uranium and thorium associated with RE deposits pose key issue with processing and disposing of waste. In United States, Molycorp mountain pass site observed for waste water and tailings as primary environmental pollution source.

Lots of attention done on environmental impacts of REEs production, distribution and politico-economics struggle to benefit the world but due to inadequate hypothetical

dynamics interplay between environment and society contributing towards human and worldwide welfare. Number of environmental and safety concerns raises in rare earth extraction because minerals containing RE ores associated with radioactive elements like uranium and thorium. Lots of management practices need like less radiation exposure to worker, public and environment, transportation, extraction, mining and waste disposal.

To reduce its effects, dams used to dispose of tailings causes increase in TDS, neutralization of HCl in water with NaOH. TDS range 10,000 mg L^{-1} with low concentration barium, boron, strontium and radiological constituents. Metals, nutrients and radiological constituents in waste water and tailings show negative impact on groundwater quality. From a social sustainability perspective point of view, ex-mining sites of REE adequately rehabilitated for other uses like Lynas corporation plant in Malaysia (Japan, 2013). REEs development put social contribution towards green economy.

In order to maintain national sustainable technology development, common insights of risks need to be balanced at site. After great centralization of supply in China, for the advancement in alternative resources efforts made on the development in USA and Australia, reduced China dominance of production of REEs to 86 % in 2012 and unconventional resources like coal, coal ash and recycling and deep sea deposits that will be examined by Japan till 2018 (Calvert, 2003, Richter et al., 2006).

For many years, human activities have been a significant source of trace metallic elements eventually contaminating the earth's surface. Such actions overburdened the regime of ecosystem in aquatic and terrestrial environments with large quantities of trace metallic pollutants and contaminants. Mining, extraction and utilization of trace elements in high value goods and as major component of infrastructure became cornerstone in human development civilization. Consequently at local, national and universal scale,

human awareness and individual role on the environmental components to manage and improve degraded terrestrial and aquatic system has been enhanced (Ozdes et al., 2011).

REEs speciation in the geochemical samples provides potential hazards and pathways for remediation. Factors like time and environmental conditions affecting speciation provide challenging and great opportunity for environmental science and technology to study rare earth elements. Evaluation of contaminants, assessment and remediation processes are recent in modern research (Ashraf et al., 2015).

Different species of ecosystem have 99 % REEs bioavailable in bound to suspended matter and sediment form. Bioavailability of rare earth elements (REEs) in different environments vary with change in ionic concentration and ligands and decrease among dissolved species as in the order: free ion, organic or inorganic complexes (Borrego et al., 2012, Sun et al., 2003). It also depends on equilibrium and change when there is a disturbance in equilibrium. Sediments may become a source of available rare earths in water which also become available to other biotic organisms feeding on them.

Hamzah et al. (2013) studied the sediments from abandoned tin mining lakes in Malaysia. Main focus of the study was to study the effect of anthropogenic heavy metals, U-238 and Th-232 in fresh water lake systems through Instrumental neutron activation analysis (INAA). Generally, synchronous higher concentrations were observed in the younger section of the cores. Mean metal concentrations for all cores for As, Cr, Mn, Zn, U-238 and Th-232 were 48.9 ppm, 41.1 ppm, 407.9 ppm, 199.1 ppm, 30.6 ppm and 85.7 ppm respectively. The results were twice as high compared to results of a control location on undisturbed land. Discharges from such activities containing heavy metals get their way into the lake through surface deposition by rain water, and remobilized from the depositional areas to the sediment coring sites. U-238 and Th-232 may be attributed to the minerals contained in the tin tailings left in the area.

Pradhan et al. (2014) studied the land subsidence in kinta valley using geographic information system and remote sensing techniques in collaboration with Department of Minerals and Geosciences, Malaysia. Urban areas and agricultural industries are the entities most affected by the consequences of land subsidence. The results indicated that the FR model could produce a 71.16 % prediction rate, while the EBF showed better prediction accuracy with a rate of 73.63 %. Furthermore, the success rate was measured and accuracies of 75.30 and 79.45 % achieved for FR and EBF, respectively.

REEs released from soil and sediments become significant as bioavailable to the algae. Sequential extraction method is commonly applied to study bioavailability of rare earths in geochemical sample analysis. Bioaccumulation of REEs in organisms depends in part upon their bioavailability. Few investigations describe the relationship between rare earth elements species and plant bioavailability. Sun et al. (2003) reported that most of the rare earths in soil and sediments are present in extractable species and increase with increase in spiking of REEs. Generally, REEs concentration in soil is very small in mg kg^{-1} (Ebrahim et al., 2009) and in plants more than 10 mg kg^{-1} (Ebrahim et al., 2009, Cao et al., 2000, 2001: Wood et al., 2004). This concentration is quite low to detect. Still no correlation in the studies found between REEs species in natural soil system and their bioavailability. The current review paper provides an overview of contents relating to geochemistry, bioavailability and speciation of REEs in the ecosystem and describes trace metal speciation and bioavailability in achieving result oriented remediation methods and risk in approaching pollution source (Haque et al., 2014).

The low concentrations of REEs (ng L^{-1} or ng kg^{-1}) hinder their geochemical fate in many environmental mediums (Kynicky et al., 2012, Williams-Jones et al., 2012). Previous research work on biogeochemistry REEs in soil/plant system and their effects on agricultural ecosystem have been widely studied (Zhang & Shan, 2001, Wyttenbach,

1998, Zawisza et al., 2011). Work done can be categorized into four phases; one include study on efficacy of rare earths based fertilizers, second geochemical behaviour of rare earth in ecosystem, third include practices employment of rare earth based fertilizer, and fourth comprises of physiological processes of enhanced yield. Ferns show high enrichment of REEs in the soil by ICP-MS and INAA which are strongly recommended techniques for such determination. Many properties of the soil such as physico-chemical, affect the exchangeable fractions of speciation which ultimately put large impact on REEs bioavailability. Study also indicates average amount REEs in the soil ranging 85-522.7 mg kg^{-1}. LREEs show abundance in the soil (83-95 %) with average value and mean ratio of 89 % and 8, respectively. Cerium is correlated with 42 % of all the REEs and 48 % with LREEs. Wheat seeds found with rare earth elements ranging from 10^{-4}-10^{-8} gg^{-1} much lower than in soil but with similar distribution. Generally in roots and leaves, rare earth concentration increase with dressing (Tsirambides & Filippidis, 2012, Skarpelis, 2002).

Lot of studies has been done on geochemistry of rare earths in different coals as potential economic value of rare earths took much attention in this century. In coal mining sector and modern technology, REEs have largely been used as tracers for diagnostic and epigenetic purposes. Some coal deposits due to different geological settings and paleoenvironments show enrichment of HREEs as compared to LREEs. Different plies from same coal due to different depositional microenvironments have variable rare earths distribution paterrens. Rare earth elements (REEs) are found bound to minerals which are associated in large extent as organics. HREEs have more organic bound affinity than LREEs and extracted humic substances found enriched with MREEs (Wenfeng et al., 2008, PePiper & Piper, 2002, Bonev et al., 2012).

Study conducted on Antaibo surface mine in China for rare earth distribution show 3 patterens: shale like, LREEs enriched and HREE rich which were recognized from peat swamps, extent of aquatic control and rare earth resources. Results indicate that extract was relatively enrich in HREEs and depleted in middle rare earth elements (MREEs) with negative anomaly. Land derived debris in major while sea water influenced organic matter with hydrogen control over the LREEs found in organic matter of coal (Bonev et al., 2012).

2.10 Speciation and Solubility of rare earth elements (REEs)

Speciation of REEs usually determines solubility and bioavailability of a substance. It depends on salinity, pH and presence of anions (Liang et al., 2005, Ashraf et al., 2015). These parameters cause difference in REEs speciation in salt water compared to fresh water which contains 70-96 % of rare earth elements (REEs) as carbonate complexes while fresh water mostly impacted by humate complexes. At high pH compared to LREEs strong complexes with carbonate ions are significantly made by HREEs as with increase in atomic number stability constant also increases whereas at low pH REE^{3+} and $(REE)SO_4^{+}$ are more common. When hydrolysis is carried out at high pH (10), different hydroxyl products of REEs such as di, tri and tetra are more common. Generally, complex formation and low solubility product (Ksp) make the solubility of REEs low. Ksp of rare earths phosphate can be as low as 10^{-25} mol^2 I^{-2} while Ksp of RE carbonates and hydroxides at 25 °C is lowest as 10^{-30} mol^5 I^{-5} and 10^{-24} mol^4 I^{-4} respectively (Liu et al., 1996). Solubility depends on pH and temperature. Each factor reduces the concentration of dissolved REEs. In broad term, freely distributed ligands in the aquatic environment are considered carbonates, phosphates and hydroxides as these decrease concentration of REEs (Delgado et al., 2012, Pfau et al., 2013, Foucault-Collet et al., 2013).

Speciation analysis is widely acknowledged in environmental chemistry as importance tool for metals state in any medium. Chemical speciation encompasses functionally and operationally defined speciation. Functionally defined speciation determines speciation for plants in exchangeable form while extractable forms of elements are determined by operationally defined speciation. Many geochemical fractions among different sequential extraction methods, established by Tessier et al. (1979) and Kersten and Forstner (1986), respectively followed by five or six steps were analyzed for metals in soil and sediments (Clough et al., 2012, Ashraf et al., 2015).

2.10.1 Speciation study in sediments

In aquatic environments, large amount of rare earths were found in the sediment bound or in suspended form. Rare earth elements (REEs) have high affinity to sediments (Li et al., 2013, Hursthouse, 2001). Distribution co-efficient of rare earth elements in suspended matter and river water is about 31 µg L^{-1} described by (Maas & Botterweg, 1993). Oceans have value around 4 µg L^{-1} with exception for Ce which is about 5 µg L^{-1} due to low solubility main form of Cerium i-e CeO_2 in which it is present in Ce^{4+} state, far away from normal trivalent oxidation states of other rare earth elements. Log Kp values (sediment to pore water) for rare earth elements are much higher than other heavy metals.

Variables like pH, salinity, organic carbon content, composition of suspended matter, Fe-Mn bound hydroxides constantly change the equilibrium among sediment, pore water and surface water due to tidal movements causing change in rare earth concentration in each partition. Rare earth elements concentration varies in the ecosystem compared to other metals. Concentration of LREEs tend to be higher than lead while Tm and Lu (less abundant REEs) have high concentration than cadmium in earth crust. Generally, odd numbered rare earth elements have lower concentration than even numbered elements. Cerium found highest in concentration while others (Tm and Lu) were two orders less in

magnitude. Main anthropogenic emission of rare earth elements are to the surface water while most lanthanides accumulated in sediments.

Wang et al. (2008) studied mining area (Antaibo, China) for the REEs in aquatic and coal organic solvent extracts. Twenty six samples were collected, analyzed by solid and organic solvent extracts on ICP-AES. Different distribution patterns were observed. The study concludes that detrimental minerals mainly control REEs in the coal but seawater has considerable effect on it (Wang et al., 2008).

Kumar et al. (2014) deliberated REEs in surface mangrove sediments from 10 locations in west coast of Malaysia by INAA technique. Samples dried, crushed to powder, and weighted for short and long irradiation time. Some specific REEs were studied. REEs concentration varies in the range 0.35-117.4 mg kg^{-1} with neutron flux of $4x10^{12}$ cm^{-2} S^{-1}. Whole procedure was done at MINT TRIGA Mark II research reactor running by pneumatic transport facility at 750 KW. Results showed 0.75-6.75 enrichment factor and high LREE abundance than HREE due to heavy mineral deposits in the study area (Kumar et al., 2014).

Leybourne and Johannesson (2008) determined REEs in 500 stream water and sediment samples by total digestion and leaching, speciation and controls over REEs patterns in surface environment. REEs were separated in oxygenated surface environment into labile (hydroxylamine) and harmful sediment fractions. Two main sources of REEs in stream sediments were found in different environments, the hostile lithologies and hydromorphically transported. Results suggest sediment organic matter and δ-MnO_2 (FeOOH) likely predominant sinks for Ce and to lesser extent to other REE in stream sediments. Results also indicate REEs normalized Ce anomalies [Ce/ Ce*] negative but Eu anomalies [Eu/Eu*] positive and NASC ranged from 0.295 to 1.77 (Leybourne & Johannesson, 2008).

Germain et al. (2009) determined the REEs in basalt, sediment, soil, ultramafic rock, and granite by spiking alkaline NaOH-Na_2O_2 and Tm and then co-precipitating on iron hydroxides in different environmental samples using ICP-MS. Nine different geological samples tested. Precision rate was found better than 10 % observed for most samples and 5 % below for the rare earth elements (Bayon et al., 2009).

2.10.2 Speciation study in soil

Speciation could be helpful in developing effective management strategies to control metal pollution in affected area. Speciation of REEs in Southern part of China with specific lateritic soil profiles was conducted. Mobilization of REEs during weathering processes is also well recognized but less data was found on REEs speciation in weathering profiles (Naji & Ismail, 2011, Aiju et al., 2012). Data analysis describes fractionation during weathering. Light rare earth elements (LREEs) leached from top zone, extremely enriched in the middle of profile whereas heavier rare earth elements (HREEs) found more depleted from bottom to top. Strong cerium anomalies found in the oxidized soil zone. Exchangeable fractions are highest carrier of rare earth elements with 40-90 % while 10-30 % is Fe-Mn bound oxides and 35 % in oxidized soil zone. Upper zone contain 10-25 % organic bound rare earths and 30 % in humus layer. Positive cerium anomaly in this zone was found with greater than 50 % exchangeable in clayey zone while up to 70 % bound to Fe-Mn oxides and in same percent ratio of Ce/Ce+ found in organic fractions. Study concludes that in soil clay minerals, Fe-Mn oxides and organic materials acts as main trap for rare earth elements and carrier of cerium anomalies.

Duan et al. (2002) determined REEs in the soil with NaOH- Na_2O_2 as flux, pre-concentration technique for co-precipitation of titanium and iron hydroxides [$Ti(OH)_4$-$Fe(OH)_3$] and ICP-MS as concise for multi element solutions batch analysis. Accuracy of the results was recognized by Chinese soil (6-samples) and sediments certified

reference materials (GSS and GSD) with less than 10 % relative standard errors. Results showed that in geological samples tightly co-existing of Ti with Nb, Zr, Ta, and Hf causes complete co-precipitation and recoveries of these metals become less with a decreased trend in basicity (Taicheng et al., 2002).

Liu et al. (2014) also determined REEs the soil with clay reference material especially GBW03102 and GBW03102a in China by using mixture of HF and HNO_3 acids in high temperatures and high pressures closed vessel digestion technique and detection of thirty seven (37) elements by ICP-MS. Results show precision lower than 5 % RSD, significantly different with reference values, reflecting the existence of >70 μm coarse grained fractions in the sample and formation of fluorides (Liu et al., 2014).

Zhang and Shan (2001) conquered REEs accumulation and speciation in wheat soil by using RE based fertilizers. Winter wheat variety, *Triticum aestivm L*. was investigated in the current study. It was found that accumulation behaviour of La, Pr, Ce and Nd change with the amount of adding fertilizers. Three distinct fractions (B1, B2 and B3) in sequential extraction procedure were separated for fertilized and unfertilized soil. Root pH and REEs soil content show considerable negative relationship for each other. Considerable amounts of REEs were also detected in roots and shoots of wheat. A significant correlation was obtained between REEs in B1 fraction and roots. In fertilized soil REEs were present in two fractions (B2 and B3) while small amount in B1. Results for lower than 20 mg kg^{-1} application of soil fertilizer indicate correlation coefficient range from 0.6519 - 0.7410 (Zhang & Shan, 2001).

Tao et al. (2005) environmentally studied (wheat and soil) the biogeochemical activities of REEs in order of their increased utilization in industrial and agricultural sectors under different soil plant system in China by INAA and ICP-MS. Results indicate mean REE soil value 176.8 mg kg^{-1} with ΣLREE/ΣHREE mean ratio of 8.0. REE in wheat

seed ranged between 10^{-11}-10^{-8} g g^{-1} in rye grass roots significantly related to soil. REEs contents in the spring wheat at maturing stage show ordered in roots > leaf > stem > crust (Liang et al., 2005).

Germund. (2004) reviewed REEs in different soil minerals with their solubility and transport in soil plant systems along distribution and localization in different organs, growth rate, crop production, plant physiology and biochemical study and soil-plant relationship and interactions. Study also focuses on some of the factors influencing adsorption and vertical distribution in soil profiles along with REE concentration. Due to weathering and leaching processes, REEs concentration in surface soil of humid climate was found lower than in parental material. Transfer ratio from soil to plant was observed low. Roots generally show high affinity than shoots and their uptake capacity was highly associated with soil acidity. Low concentration of REE favors plant growth and productivity. Due to increased analytical techniques in environmental sciences, addition of REEs based fertilizers to soil and in both pedagogical and physiological processes contribute great interest for trace metals (Tyler, 2004).

Zhang et al. (2001) made possible the use of RE oxides (REO) in soil accumulation and destruction as tracers by examining their binding capabilities and quick acid extraction procedures. It is well known that direct mixing of REOs do not change the physicochemical properties of soil. In the current study, five REE oxides in powder form were assorted in Miami soil (silt loam) for REEs mobility by simple acid leaching method. Samples analyzed on ICP-MS showed maximum co-efficient of variation < 10 % for all REEs. Results also indicate direct application of REE oxides would be better comparative to other REEs (Zhang et al., 2001).

Xinde et al. (2001) studied the REEs released from soil for their effect of redox potential and pH. Three pH values 3.5, 5.5, 7.5 along with redox potential of 400, 0, -100

Mv applied by introducing two gases such as oxygen and nitrogen into the soil solution. Results showed rapid release of LREEs, correlated positively under low pH conditions and reduction with Fe-Mn indicating might due to Fe-Mn oxyhydroxides but Ce remarkably influenced by redox potential. Low pH and redox potentials found more favourable. In solid phase exchangeable fractions, contents of LREEs and Fe-Mn fractions decrease as pH and redox potential decrease from soil solution (Cao et al., 2001).

Mobility of rare earths largely depends on chemical speciation in weathered profiles. Ground water chemistry, sediment provenance and chemical weathering of soil and sediments is achieved by distinctive features of REEs (Ding et al., 2001, Nyakairu & Koeberl, 2001). Rare earths and other element deposits exist in ocean from 3500-6000 meters below sea level containing 80-100 billion tons of REEs (Ragheb, 2014). LREEs enriched in kimberlite rocks extract by acid leaching of mantle under the action of fluids rich in H_2 and CO. Some kimberlite show high concentration of HREE due to the presence of xenogeneic grains of garnet. Geochemistry of REEs in kimberlite rocks is obtained by using ICP-MS (Bogatikov et al., 2004). On industrial scale, REEs produced from rare earth flurocarbonates termed bastanasite. 50 % REEs found in thorium re-phosphates termed as monazite (Richter et al., 2006). Both minerals provide LREEs and 95 % of currently utilized REEs. Bastnasite occur in calcium-silicon rich rocks while monazite and xenotime occur in low ca-granitoid rocks and pegmatite's (Chengdu, 2005).

Different concentrations of REEs found in different types of Chinese soil, reported values ranged in ppm in soil to ppb in plants. Concentration of REEs in plants ranged from less than 1 ppm to 15,000 ppb distilled water and La from 88 to 15,000 ppm distilled water (Kabata Pendias & Pendias, 2001). About 200 rare earth oxides species have been found up till now. LREEs mostly deposits in carbonates and phosphates while HREEs were found in titanates, tentalates, niobates and phosphates. Global REEs deposits

classified as igneous, sedimentary and secondary types. Largest REEs deposit in China, Bayon Oboyo, located in Magnolia formed by hydrothermal replacement of carbonate rocks. Mountain pass in United States, Maoinoing in China and Mount weld in Australia are worlds rare earth resources constitute by carbanatite deposits (Kanazawa & Kamitani, 2006).

2.11 Bioavailability and uptake capacity of REEs

REE widely distributed in the biosphere. REEs can be accumulated in different areas of the environment following anthropogenic inputs because of the low mobility of these elements. Life processes (physiological and biochemical) of plants, soil and living organisms effected by rare earth elements (Liu et al., 2011, Laveuf et al., 2008, Rollinson, 2014, Balabanova et al., 2013, Balabanova et al., 2015). There is a scarcity of information on REE bioavailability in soil. REE content in soil range from 30-700 mg kg^{-1} (Bohn et al., 1985) move through roots and above ground organs in plants. Cerium, as the most dominant of the REEs, shows a certain variation compared with data from similar investigations; for example, in Australian soil Ce ranges from 21.0 to 120.3 mg kg^{-1} in Japanese soil it ranges from 2.46 to 116 mg kg^{-1} and in Swiss forest soil it ranges from 10.4 to 100.8 mg kg^{-1}. The contents of La in *E. citriodora* planted in La-treated soil were significantly higher than those grown in soil without addition of La. This implies that the plant could take up La.

REEs automorphic and alluvial distribution in soil (top, sub-soil samples) in the environs of Bregalnica River was studied by Balabanova et al. (2015). LREEs were predominantly related to the Quaternary terraces and the Paleogene flysch. The mean value of the sum total of rare earth elements (ΣREEs) was determined to amount to 79.3 mg kg^{-1}. The content of the light rare earth elements (LREEs) in the whole investigated

area ranges from 8.6 to 225 mg kg^{-1}, while the content of the heavy rare earth elements (HREEs) ranged 0.92 - 33.7 mg kg^{-1} (Balabanova et al., 2015).

Bioavailability of REEs in the soil depends in exchangeable fractions range from trace to 24 mg kg^{-1} and water soluble content from 10-20 mg kg^{-1} (Zhu et al., 1997). Physicochemical properties of the soil (Liang et al., 2005) including soil cation exchange capacity (Li et al., 2001, Alonso et al., 2004), pH, organic matter, and organic acids controls REE distribution and transformation. At a higher pH level, the immobilization by soil found more rapid, and insoluble compounds would be formed when REEs reacted with hydroxides or oxides. However, at low pH, they dissolved and so released the bound REEs (Shan et al., 2002, Ghaderi et al., 2012).

In extracted soil, REE fractions are; water soluble fractions, carbonate bound fractions, the exchangeable fractions, the sulphide bound fractions, the Fe-Mn oxide bound and organic matter and residual fractions (Wang et al., 2001, Wali et al., 2014). Higher concentration of Rare earths in the soil may cause changes in the ecological system of microorganisms. REEs concentration in soil solution mostly controlled by adsorption and desorption process, acts as indicator of bioavailability of rare earths (Wang et al., 2003). Fast reactions of REE with soil followed by sorption but slow desorption rate results in low bioavailability with time and reduced uptake by plants.

Mobility differs in different parts. The total REE concentration not only included the portion available to plants, but also those strongly bound within crystal structure of soil. EDTA enhances the REEs uptake. Degree of translocation of REE in plants is 20 %, mostly present in roots, in intracellular and extracellular parts forming chelates with the components of metabolism (Tai et al., 2010). REE in plants stimulate uptake of certain elements, act like calcium by inhibiting calcium uptake. REE also effect enzyme activity, production and intensity of photosynthesis, content of phytohormones, water regime of

plants and water deficiency resistance and put favorable effects on seed germination (Liu et al., 2014). Some crops like sugar cane, sugar beet, rice favorably affected by REE. Rare earth elements in the grass roots depend on soil. Lots of research on biogeochemical behaviors (Zhang and Shan, 2001) and effect of REEs on agricultural ecosystems divided into four periods include; study on the efficiency of REE based fertilizers, geochemical behavior of REEs in ecosystem, practices on employing REE based fertilizers and physiological process of enhanced yield. REEs based fertilizers applied on tea plant for 25 days suggest REEs bound with polysaccharides which decreases with time (Wang et al., 2003). Rare earth based fertilizers show increased concentration of REE in roots, stem and leaves (Wen et al., 2001). REE content in wheat seed ranged between 10^{-11}-10^{-8} g g^{-1} (Liang et al., 2005). Every year about 50-100 million tons of REE based salvolatile and phosphate fertilizers enters the agriculture system causing adverse health effects and detrimental environmental issues through bioaccumulation through the food chain (Xiong et al., 2001). A lower pH favors the uptake of REEs by plants. Rhizosphere has a lower pH than the soil far away from plant roots as root secretes acidic substances such as organic acids to facilitate the metal uptake. The result of present study shows that the final pH was lower than the pre-set pH which may be explained by the secretion. This would help the dissolution of metals so more REEs appeared as free ions for plant assimilation. Organic matter in soil plays an important role in providing REEs to plants. Dissolved organic matter had the highest affinity to REEs and was easily assimilated by plants.

A study conducted by Tyler (2004) in a forest in Germany comprises different varieties of plant materials and concentration of all REEs was also reported. Commercially grown cabbage (*Brassica oleracea var. capitata*), show very low concentration with transfer factor 0.04-0.09 and also *Agrostis capillaries* were also found with low concentrations. However, roots of plants such as maize and mungbean indicate

20-150 times high La if grown in culture media (Tyler & Olsson, 2001) while rice and pea plants roots significantly show only lanthanum and ytterbium in the xylem and endoderm (Tyler, 2004). Pteridophytes (ferns) are also well known as RE accumulators. In Japan 96 fern species also show positive correlation between lanthanum and cerium (Ozaki et al., 2000). Norwegian mosses containing La and Y indicate their main origin from windblown minerals particles with less contribution from anthropogenic pollution. Mesophyll tissue of leaves found accumulated with lanthanum (10– 40 μg g^{-1}) whereas cerium (3–30 μg g^{-1}). *Eichhornia crassipes* root hairs adsorb Eu^{3+} on their root hairs surface. This is also supported by the fact that carboxyl acid groups bind the Eu^{3+} on root hair surface (Kelley et al., 2000). Eu^{3+} has been found in a tendency to combine with carboxylic and phosphate groups in *Pseudomonas aeruginosa* (Tyler, 2004).

Summary

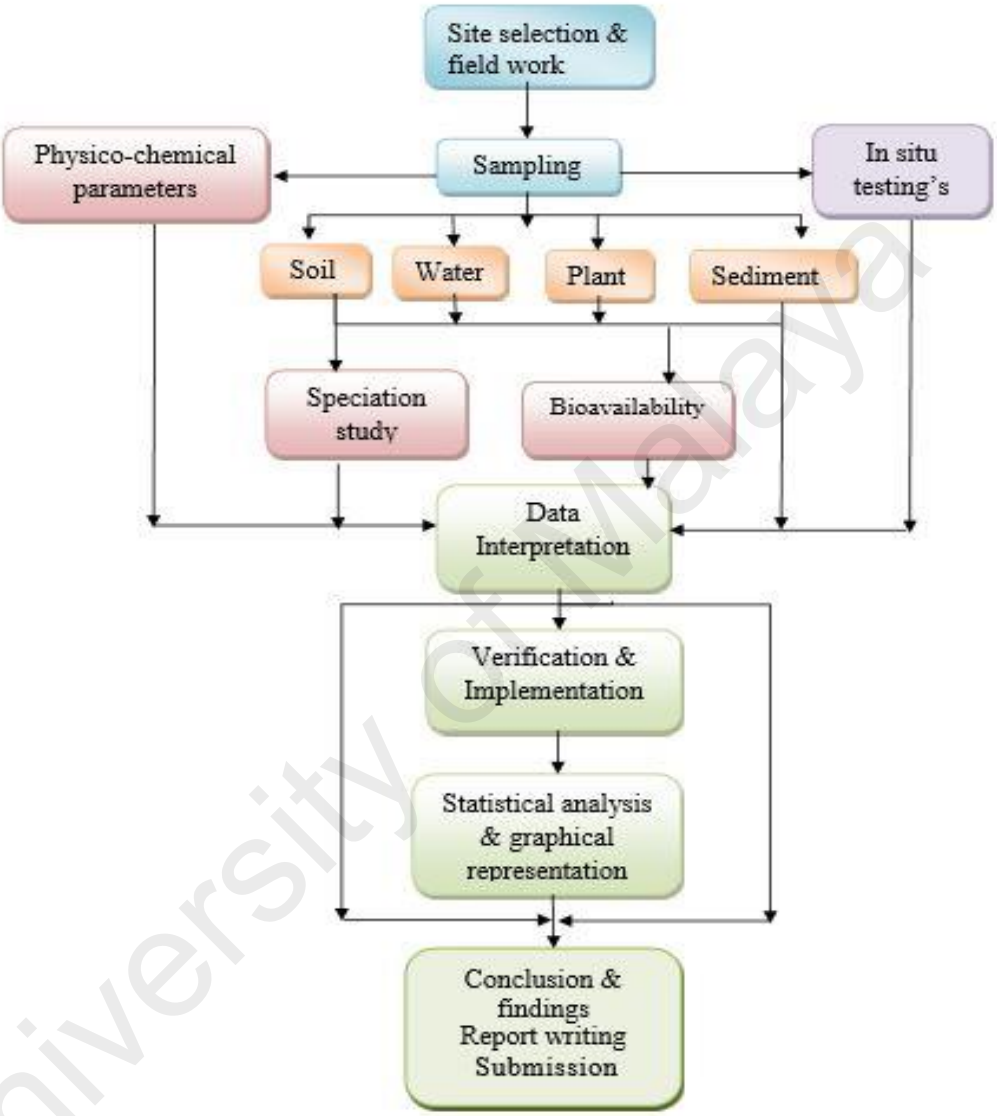
In this chapter literature related to REEs, their sources, characteristics, global production, distribution has been discussed in detail. Different determination techniques used for REEs have been described as well. Environmental impacts of REEs have been given in detail in the light of different environmental media and mining. Speciation study related to previous literature has been highlighted for sediment and soil. Bioavailability and potential mobility of REEs in the plants has also been deliberated. The chapter basically reflects the overall literature of the previous work done but there are not enough data which deeply explains the speciation, bioavailabilitiy, uptake capacity and potential mobility of REEs. The current study has been focused mainly to find the speciation and bioavailability of REEs.

CHAPTER 3: METHODOLOGY

3.1 Introduction

Water is an important tool for sustaining life on earth. Terrestrial and aquatic ecosystems are more related to the quality of water for giving habitat to living organism and aquatic fauna. Water quality is mostly related to the geology, morphology, rainfall, sunshine, climate etc. Different parameters such as pH, electrical conductivity (EC), cation exchange capacity (CEC), organic matter (OM), total dissolved solids (TDS), total suspended salts (TSS), moisture content (MC), anionic analysis provide difference in water quality criteria for a similar water bodies. Mining activities have major impact on water table disturbance and diversion from source.

Sediments have been an important part of aquatic media, acting as a source of many metals whether beneficial or harmful for aquatic biota. Soil is a medium where most of the metals could be found. Plants growing on the soils from the mining site have been utilized for many purposes. Up till now most of the work has been done to determine their concentration in different samples using different detection techniques. This chapter discusses the complete methodology that had been adopted to determine the amount, concentration and toxicity of rare earth elements with special emphasis on its speciation and bioavailability using the most sensitive and accurate technique of ICP-MS. In mining area of Lahat Perak, Malaysia for the first time this study has been done. Instruments used and techniques applied have been described in details. This chapter covers the whole period of research starting from fieldwork to collection, treatment and analysis of samples. The current research work follows the plan given as a research methodology flow chart shown in **Scheme 3.1**.



Scheme 3.1: Flow chart of the research methodology.

3.2 Sampling location

In this work, four types of samples were collected during the sampling trips which are water, sediments, soil and plants **(Appendix A).** The site selection is the ex-mining area in Perak. Sampling location map is shown in **Figure 3.1**. Sampling was done from December 2014 to February 2016. Sample collection was done for three times after every 6 months for three consecutive days.

3.3 Pre-sampling preparation

For water sampling 2 L plastic bottles were first soaked in 10 % nitric acid overnight. Then the bottles were washed with distilled water and dried. Distilled water, gloves, masks, lab coats, safety belts, batteries, notebook, tagging tapes etc were also kept. For *in situ* measurement of different parameters for water samplings Hydrolab DS5 (Hydrolab), portable pH meter (Orion Star A214, Indonesia), dissolved oxygen meter (Europe) and Van Dorn horizontal (KC-Denmark) water sampler were used. For sediments collection grab sampler (Wildco instruments, Petile Ponar-USA) was used. Soil samples were taken by digging the soil from different depths using auger.

3.4 Sampling and Preservation

Water samples from the mining lake were collected using Van Dorn horizontal (KC-Denmark) water sampler in 2 L plastic bottles. The sampler was made of sturdy transparent PVC and had a double release valve, activated by a drop messenger. The sampler had a capacity of 5 L in water boat. From each location, two bottles of water samples were collected. One used as pure for anions analysis while other preserved with 3% nitric acid. The bottles were kept in cooling boxes during the sampling trip.

After collecting samples, the initial parameters such as pH, dissolved oxygen, specific conductivity, temperature, salinity, total dissolved salts (TDS), ammonium ions, oxidation reduction potential and nitrates were measured *in situ*. pH and DO were

measured using portable pH meter (Orion Star A214, Indonesia) already calibrated while all other parameters were measured using multiprobe Hydrolab DS5 (Hydrolab) which was already calibrated using calibration standard solutions. The Hydrolab was calibrated again after taking samples from three sites or after three hours interval and electrode was rinsed before and after every reading with deionized water to keep the accuracy and precision in the measurements.

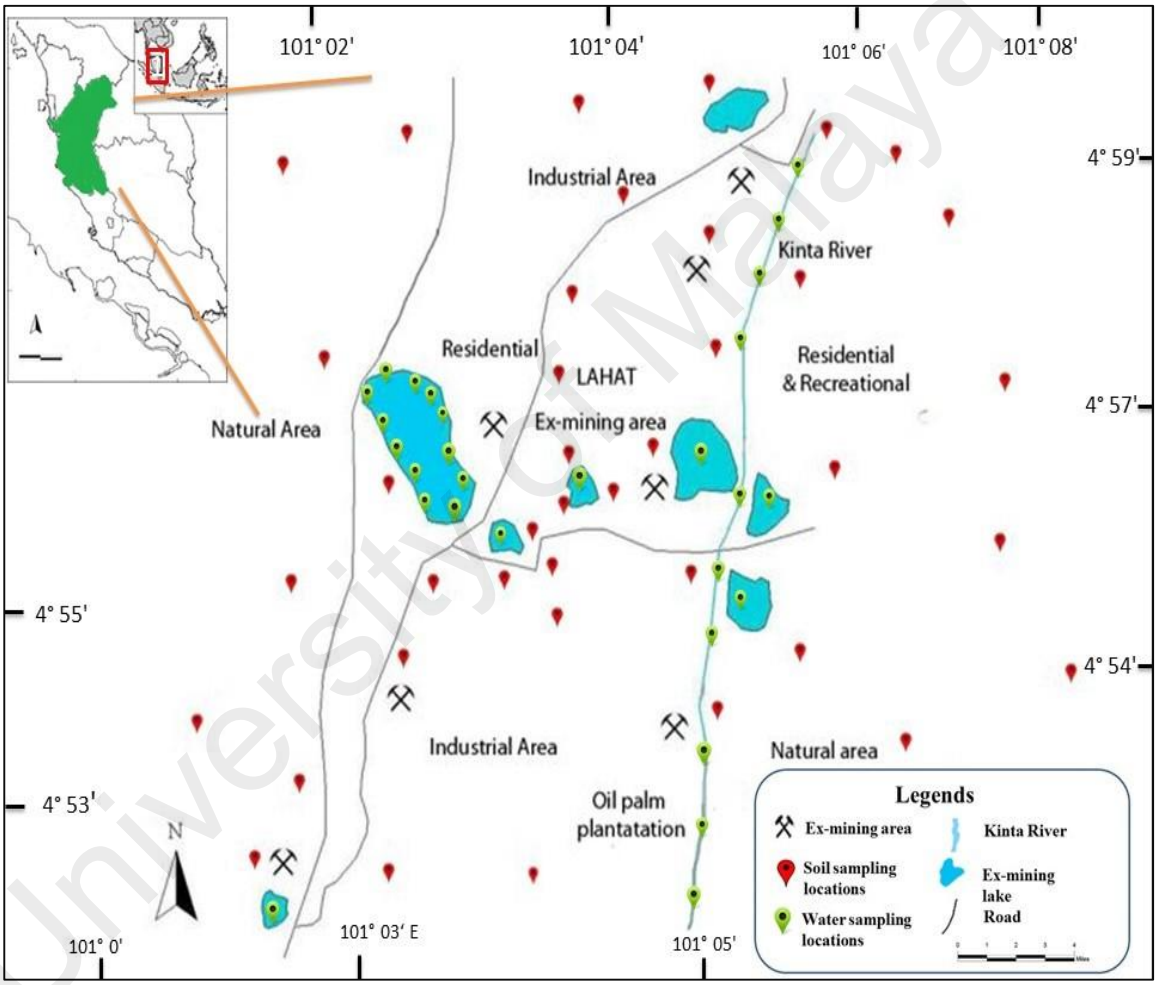


Figure 3.1: Map showing sampling stations from the study area.

Sediment samples were collected using Grab sampler according to pre-planned sampling locations from the lake. During the sampling, sediments were not found from Kinta River. Only ten sediment samples were collected from the ex-tin mining lake but

the sedimentation rate was low. On one side of the lake high mountain range is present. These mountains due to heavy rainfall and high erosion rate together with reclamation activities cause sedimentation rate high but low towards the lower part of the ex-tin mining lake. After collecting the samples were kept in polyethylene plastic zip bags and put in cool box and transferred to the laboratory.

Soil samples have been collected from residential, mining, industrial, oil palm plantation, recreational and natural regions located in the west of state of Perak in Peninsular Malaysia consisting of Lahat, Menglembu, Kinta valley, Batu Gajah, Kampong Sri Kinta in three different depths of surface soil (0-20 cm), deep soil (21-40 cm) and deeper soil (41-60 cm) using an auger as illustrated in **Figure 3.2.** After samplings, the samples were stored in polyethylene bags, kept in the cool box and transferred to the laboratory for further analysis. All soil samples were air dried, grounded and sieved through <150 µm sieve to obtain homogeneous particle size and finally stored prior to analysis.

Figure 3.2: Soil sampling activity in the study area.

Most of the plants were collected from sampling stations where soil was taken. Plant samples were dug using scrapper from the roots and whole plant was collected. As samples collected from each location, they were tagged and then put in plastic bags and stored in cool box till taken to the laboratory. Sampling parameters have been given in detail in **Appendix A**.

3.5 Water analysis

3.5.1 Determination of anions in water using IC

Water samples collected from lakes and river were first filtered and sent for anionic analysis by using ion chromatography-IC (861 Advanced Compact- Metrohm, Switzerland) as shown in **Figure 3.3**. Fluorides (F^-), chlorides (Cl^-), nitrites (NO_2^-), bromides (Br^-), nitrates (NO_3^-), phosphates (PO_4^{3-}) and sulphates (SO_4^{2-}) were analyzed. Multielement IC-standard solution was used from 5 mg L^{-1} to 30 mg L^{-1} for all the anions. Sample volume used was 2 mL and total running time for single sample determination was 17 minutes. The results were obtained in the form of spectra showing concentration of all these anions in a single sample.

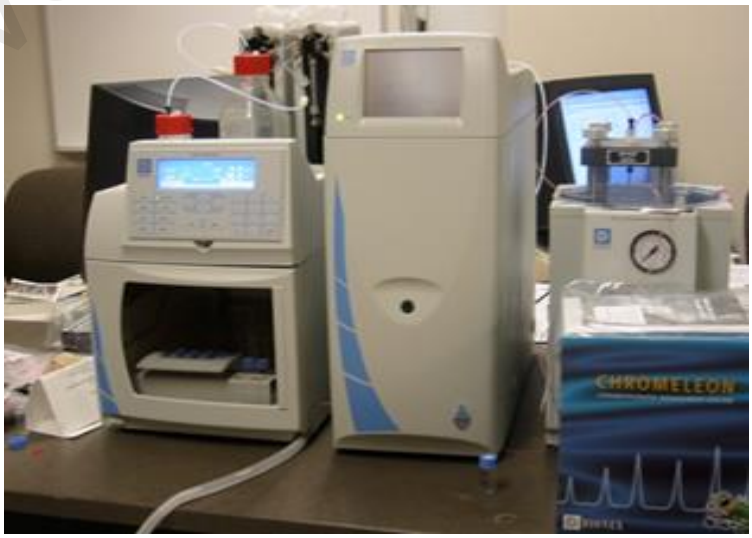


Figure 3.3: Anionic analysis for water samples collected using ion chromatography (IC) (861 Advanced Compact- Metrohm, Switzerland).

3.5.2 Determination of REEs in water using ICP-MS

For sample preparation, water samples were first acid digested through microwave digester using three different combination of volume of acid. Firstly, 5 mL of sample and 1 mL of HNO_3 and second combination of 5 mL of sample and 2 mL of HNO_3 and then third combination 5 mL of sample and 3 mL of HNO_3 using temp 90 °C for 20 minutes. After adding sample and the reagents, the vessels were capped tightly and put in a microwave digester for the acid digestion using power time system for 20 minutes. After completion of the digestion, the vessels containing digestate were taken out from the microwave digester and kept in fume hood, cooled and slowly released the pressure to open the vessel. Then, the samples were shifted to centrifuged tubes graduated up to 50 mL and three times washed with deionized water for 20 minutes at 2800 rpm to remove and undissolved solid particles.

The solution obtained should be very clear not to affect the nebulizer of the ICP-MS instrument. Comparing the results for all three combinations, first combination found suitable and best to run samples as it gives maximum output with minimum amount of acid. This combination was found green environmentally as acid is used in very less quantity but gives better results. To validate the method, SRM 1643e (Trace elements in water- NIST) was used throughout this work. In this study, CEM-Mars Xpress (CEM cooperation, Matthews, NC.U.S.A) was used to digest the water samples as shown in **Figure 3.4 (a)**.

Water samples in this research were analyzed using ICP-MS 7500ce Agilent as shown in **Figure 3.4 (b)**. All calibration standards were prepared from the Agilent multi element calibration standard 8500-6944 containing Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Y, and Yb in 5% HNO_3. All the standards were diluted by ultra-pure water for determining the concentration of elements in the digested soil samples.

For linear calibration plot, five standards namely 10, 30, 50, 75 and 100 ng ml^{-1} were prepared. In the calibration plot the correlation coefficient was from 0.994 to 0.996 depending on the element.

(a) (b)

Figure 3.4: (a) Microwave digester CEM-Mars Xpress (CEM cooperation, Matthews, NC.U.S.A) for acid digestion of samples (b) ICP-MS (Agilent 7500ce-USA) for rare metal analysis.

3.6 Sediment analysis

In laboratory, the sediment samples were stored at 4 °C until analysis. For the pre-treatment, the samples were dried by heating in oven at 60 °C for about two days then, the samples were sieved using 2 mm steel sieve to obtain homogeneous particle size. Particles bigger than 2 mm were discarded. Finally, the samples were kept in the plastic containers prior to analysis.

3.6.1 Determination of anions in sediments using IC

After obtaining the homogeneous size, 5 g of sediment samples were agitated with 25 mL of water for 8 hours and then centrifuges at 2800 rpm and decant the supernatant liquid. 15 mL of this sediment solution was sent to analyze anion in Ion Chromatography (IC). Procedure for IC analysis is same as described earlier in section 3.5.1.

3.6.2 TOC measurement

For TOC analysis of sediments, fresh solutions of the sample were prepared using the same method as for anionic analysis. Then the samples were run using TOC analyzer (SHIMADZU-North America) to determine total organic carbon in the samples.

3.6.3 Determination of REEs in sediments/soil using ICP-MS

For sample preparation, 1 g of sediment/soil sample was first acid digested through microwave digester CEM-Mars Xpress (CEM cooperation, Matthews, NC.U.S.A) with 3 mL HNO_3 and 2 mL of H_2O_2 using pressure time system. After adding soil sample and the reagents, the vessels were capped tightly and put in a microwave digester for the acid digestion using power time system for 20 minutes. After completion of the digestion, the vessels containing digestate were taken out from the microwave digester and kept in fume hood, cooled and slowly released the pressure to open the vessel. Then, the samples were shifted to 50 mL graduated centrifuged tubes, diluted and centrifuged for 20 minutes at 2800 rpm to remove undissolved solid particles. The solution obtained should be very clear, so that it does not affect the nebulizer of the ICP-MS instrument.

To check the accuracy of sediment samples SRM 4354 (NBS) was run using the same method as described above while for the soil SRM NIST-2586 was used. Samples were prepared in triplicate to get better results. After digestion samples were diluted to 50 mL and then analyzed by ICP-MS.

Sediment/soil samples in this research were analyzed using ICP-MS 7500ce Agilent. All calibration standards were prepared from the Agilent multi element calibration standard 8500-6944 containing Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Y, and Yb in 5% HNO_3. All the standards were diluted by ultra-pure water for determining the concentration of elements in the digested soil samples.

For linear calibration plot, five standards namely 10, 30, 50 75 and 100 ng ml^{-1} were prepared. In the calibration plot the correlation coefficient was from 0.994 to 0.996 depending on the element. From the results the concentration of REEs was determined.

3.7 Soil Analysis

Different initial physico-chemical parameters for soil were determined as follows:

3.7.1 Grain Size

For the particle size determination, electrical sieving method was used. In this method, 100 g of each soil sample was sieved using sieves ranging in size from 3.35 mm to < 0.063 mm. Running time was 20 minutes for each sample. After sample run, the soil obtained from all sieves including pan was weighted. The same procedure was repeated for all soil samples. Finally, the percentage of each soil fraction was determined to provide composition data of gravels, silt, sand and clay in soil samples taken from study area.

3.7.2 Colour

Colour of soil has been observed using Mansell colour chart.

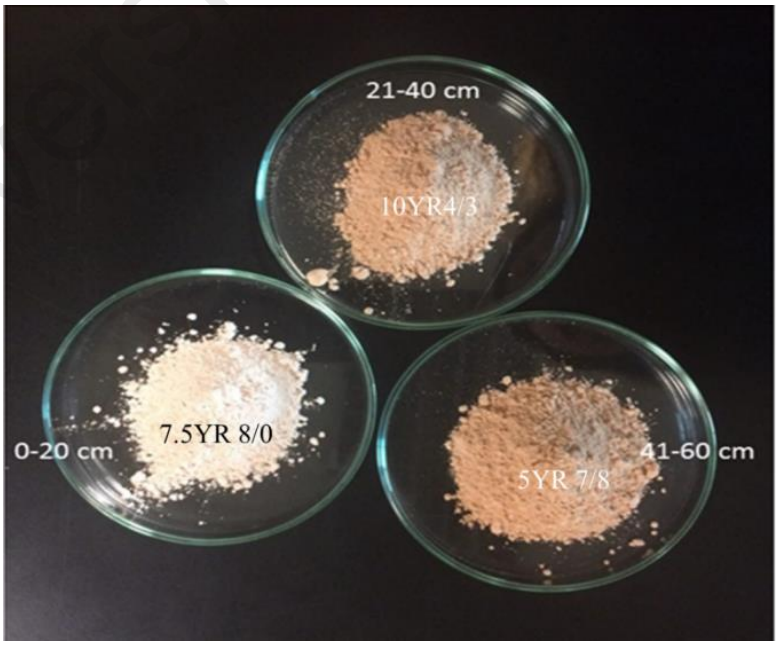


Figure 3.5: Variation in colour of soil samples collected from three different depths.

3.7.3 pH

pH of the soil was determined by using deionized water in 1:1 ratio. Mixture of soil and water will be shaken on horizontal shaker for 5 hours. Then the solution was centrifuged at 2800 rpm for 10 min. the supernatant was decanted and pH was measured by portable pH meter (Orion Star A214, Indonesia). The same procedure was repeated for all the samples.

3.7.4 Electrical Conductivity (EC)

Electrical conductivity of soil was determined using the sample solution as for the determination of pH. For the measurement of EC, fresh soil sample solutions were be prepared. Electrical conductivity meter (Orion Star A112, Indonesia) was used for Ec determination.

3.7.5 Cation Exchange Capacity (CEC)

CEC for soil was determined by a novel method using sorption technique. 1.0 g of soil samples was adsorbed with 10 mL of water and 100 ppb standard multielement solution on horizontal shaker for 1 hour. Samples were taken out after every five minute interval, centrifuged and then analyzed on ICP-MS. Secondly same procedure was repeated for CEC by using 1 M HCl. Soil samples were first soaked in 1 M HCl, stay for 1 hour then washed three times with HCl and further used. After repeating same procedure comparison was done in the results obtained after ICP-MS and found the cation exchange capacity of soil.

It is consider that the active mineral has the formula of R—X. R may be an anionic compound or ligand and X as cation part. Chemical reactions taking place are shown in Equation 3.1, 3.2 & 3.3**.**

First acid was added to the mineral

$$R—X + H^{+} \leftrightarrow R—H + X \quad \text{(Equation 3.1)}$$

Then R—H can act as cation exchanger with most of trace elements "$_{M}Y^{n}$" in the form of their cations. For simplicity, called as Y then

$$R—H + Y \leftrightarrow R—Y + H^{+} \quad \text{(Equation 3.2)}$$

It was expected that the mineral can be recovered by washing it with acid

$$R—Y + H^{+} \leftrightarrow R—H + Y \quad \text{(Equation 3.3)}$$

3.7.6 Moisture content (MC)

Moisture content of soil was taken by using furnace (LT1200-6, Germany) as shown in **Figure 3.6**. First an empty crucible was taken and was weighted. Then some wet soil was put into the crucible and weighted. Then, subtract the total weight of wet soil and crucible from empty crucible. The crucible with wet soil into oven for drying at 105 °C and medium power overnight. The crucible was removed and weighted at ambient temperature. The mass of dry soil with crucible from the empty crucible was subtracted and divide to the dry soil mass by the wet soil and multiplied with 100 to give the moisture content of the soil samples. The same procedure was repeated for all soil samples.

3.7.1 Organic matter content (OM)

For determining the soil organic matter (OM), a very precise and accurate method developed by Walkley Black (WB) was used in this study (Gelman, Binstock, & Halicz, 2012). In this method dichromate solution is used to oxidize organic matter content of the soil. After completion of oxidation, titration is carried out. Titration involves dichromate and ferrous sulphate solution in specific volume (mL). After completing titration, organic matter content (OM) was calculated by taking the difference between amounts of dichromate solution added against volume titrated.

Figure 3.6: Furnace (LT1200-6, Germany) used for moisture content analysis.

To clearly observe the end point stirring plate with light was used. Reacting reagents were prepared by using careful and safe methods. Potassium dichromate 0.16 M solution was prepared by adding oven dried or desiccated 98.08 g and mixing in 1-2 L ultrapure water. Ferrous sulphate 1.0 M was prepared by mixing 556 g in 1500 mL ultrapure water. After that, 30 mL of concentrated sulphuric acid was added, diluted up to 2 L and cooled. After cooling, the solution was kept in a container not more than a month for the analysis. Before titration, wash and clean al the apparatus such as tubing's, burettes and stopcock with deionized water and dried.

To carry out titration for soil organic matter determination, burette must be rinsed thrice with $FeSO_4$ and then blank can be run. 1.0 g of dried soil sample was added in a wide mouth graduated Erlenmeyer flask (250 mL). Before running the sample check the

accuracy and standardization of ferrous sulphate by running blank samples twice. Difference in the measurements of two blanks taken must be around 0.2 mL. If such results are not obtained then clean the burette again and repeat the blank samples to avoid the error. 10 mL of potassium dichromate solution was pipetted in a volumetric flask (250 mL). Soil sample was added in the flask and was shaken gently to mix the soil material. This flask was placed in a fume hood and then after some time 20 mL of conc. sulphuric acid was added and mixed with care. The flask was kept under a fume hood to keep the solution to room temperature. Then few drops of Phenanthroline complex (as indicator) were added and titrated with ferrous sulphate solution immediately. Stirring plate with lighting was used to observe the color change and complete mixing.

During titration as reaction proceeds colour of solution changed from reddish brown to green and then on abrupt change to reddish brown that showed the end point. Finally difference in the volume of ferrous sulphate solution used was noted before and after the titration and difference was calculated. Calculation for OM content of soil was done as follows using Equation 3.4.

$$\text{Organic matter (\%) of soil} = (1 - S / B) \times 10 \times 0.68 \qquad \text{(Equation 3.4)}$$

Where S is amount of $FeSO_4$ used in titration, B is average $FeSO_4$ for both blanks, 10 is conversion factor and 0.68 is factor for converting organic carbon to organic matter.

3.7.2 XRF analysis

Xray fluorescence spectroscopy (XRF) (PANalytical- Netherlands) was employed to find out the percentage of elements in soil samples of the study area. 20 g of each sample was sent to XRF analysis and then results were evaluated for REEs and major elements.

3.7.3 Determination of REEs in soil using ICP-MS

Same as described earlier in section 3.6.3.

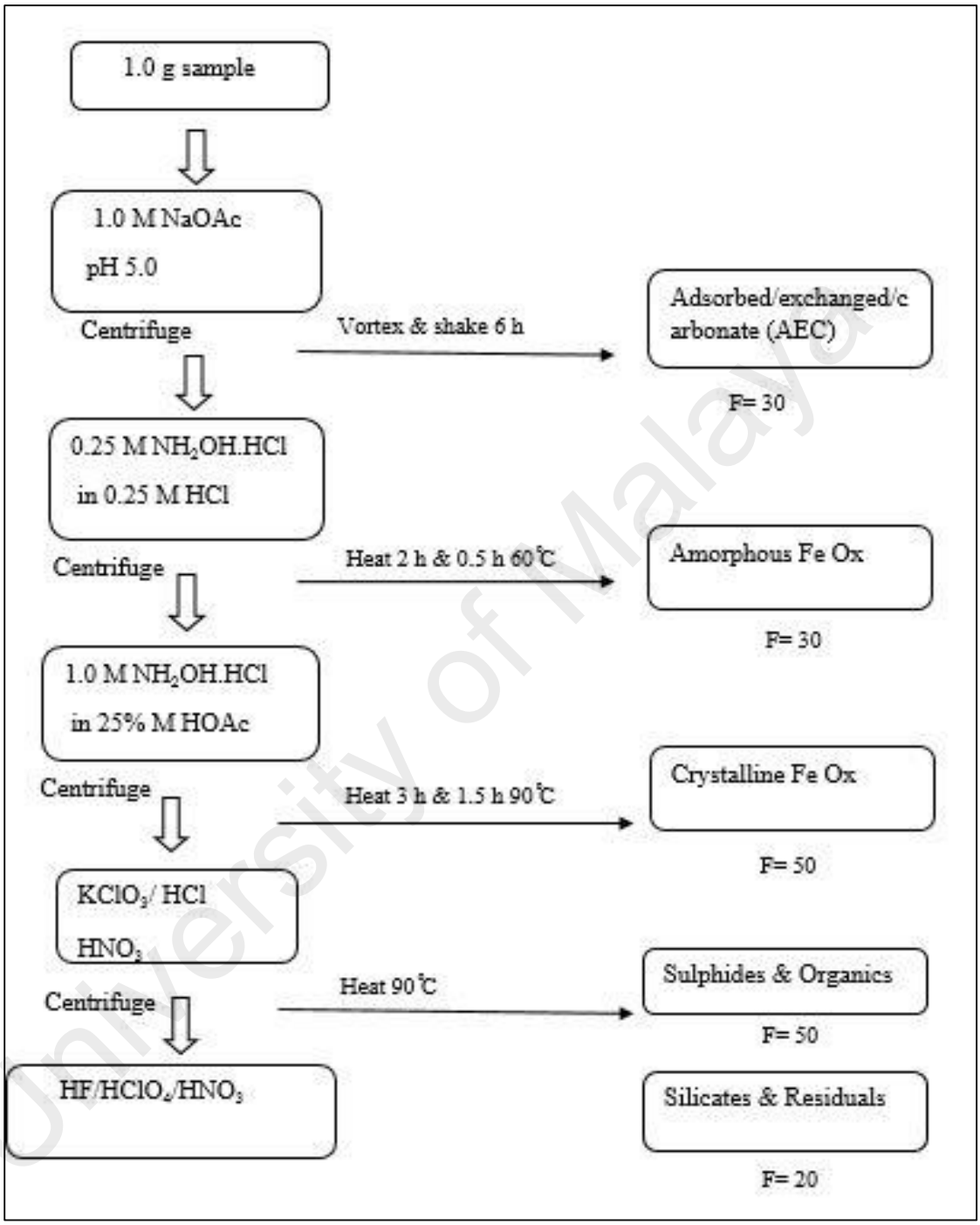
3.8 Speciation study of REEs in sediments and soil

A sequential extraction scheme for sediment and soil applied in the study described by Hall et al, (1996) as shown in scheme 2. This procedure was modified to obtain maximum output from different steps. Continuous shaking was provided in each step, resulting in higher concentration of the analyte. In previous studies agitation during different stages of extraction was provided for specific times but it was observed that maximum amount of analytes with good accuracy is achieved if agitation is provided continuously. The phases selected for extraction categorized into five steps (i) adsorbed/exchangeable/carbonate (AEC) (ii) Fe oxyhydroxide (amorphous) (0.25 M NH_2OH.HCI) (iii) Fe oxide (crystalline) (IM NH_2OH. HCI) (iv) sulphides and organics ($KClO_3$/HCI) (v) silicates and residual (HF-$HClO_4$-HNO_3-HCI).

Generally, all five steps consist of 22 sub steps to complete extraction for single sample. First three stages represent two extracts. Further application of sequential scheme to all sediment and soil samples demonstrate that summation of elemental concentrations compared favorably with those values obtained by direct acid digestion involving less material lost during the sequential procedure. The whole procedure was modified for REEs as follows.

3.8.1 Fraction I: AEC (adsorbed / exchangeable / carbonate) phase

Soil samples (1 g) were extracted at room temperature using 20 mL 1.0 M CH_3COONa at pH 5, vortex and agitated on horizontal shaking for 6 h as shown in **Figure 3.7 a**. Extracted samples were centrifuged for 10 min using 2800 rpm, decanted the supernatant and residue twice treated with 5 mL of water, vortexed, centrifuged, repeat the whole procedure to get maximum leach of the residue and finally analyzed.



Scheme 3.2: Schematic diagram for sequential extraction procedure where F represents dilution factor (Hall et al. 1996).

Figure 3.7: Laboratory work during speciation study (a) horizontal orbital shaker (TS-560, Taiwan) (b) Hotplate with stirrer (SP 131320-33- USA).

3.8.2 Fraction II: Amorphous Fe oxyhydroxides (Am Fe Ox)

The residue from fraction I was vortexed as shown in **Figure 3.8 (a)** with 0.25 M hydroxylamine hydrochloride in 0.25 HCl using 20 mL, then placed in oil bath for 2 h with continuous agitation at 60 °C on hot plate with stirrer as shown in **Figure 3.7 (b).** After that centrifuged as shown in **Figure 3.8 (b)** the sample about 10 minutes and supernatant liquid was decanted and put into labeled test tube. Residue was rinsed, vortexed and centrifuged twice. The second leach of residue was carried out with 0.25 M $NH_2OH.HCl$ but heat only for 30 min.

3.8.3 Fraction III: Crystalline Fe Oxide (Cry Fe ox)

Residue from fraction II was vortexed with 30 mL of 1.0 M $NH_2OH.HCl$ in 25% CH_3COOH and placed in oil bath for 3 h with continuous agitation for homogeneous media during leach process at 90 °C. Then again centrifugation was done and supernatant decanted volume made up to 50 mL and analyzed. The same procedure was replicated but this time heat for 1.5 h only and finally analyzed.

3.8.4 Fraction IV: Sulphides and organics

Residue from fraction III was vortexed with 750 mg of $KClO_3$. Then 10 mL of HCl was added, again vortexed and paused for 30 min. After that 15 mL of water was added, vortexed and centrifuged followed by decantation of supernatant to labeled centrifuged tube. Then 10 mL of 4.0 M nitric acid was added to the residue obtained from the last step, again vortexed and heat on water bath at 90 °C for 20 minutes. When time passed, all of the material transferred to Teflon pressure tubes and the same procedure was repeated and added to test tube containing $KClO_3$/HCl extractants with this HNO_3 leachate. Washing was done as before and sample get ready to analyze. For absorbing REEs from the medium some of rare metals oxides acts as good substrate having greater surface areas. On such metals, REEs bound by complexation or by bioaccumulation through organic matter, surface coatings and living organisms. Such metals on oxidation could leach from their respective materials.

Figure 3.8: (a) Sonicator (LUC-405) (b) Centrifuge (Megafuge 8-Germany) used during speciation study.

3.8.5 Fraction V: Silicates and residual oxides

Residue from fraction V placed on an insulating heating system with 2 mL of 16 M HNO_3 at 200 °C till volume makes up to 0.5 mL. 2 mL of 12 M HCl was added as solution become cool and keep on hot plate for 20 min at 90 °C. Then the sample was cooled and 10 mL of mixture of acids was added; HF (5 mL)/$HClO_4$ (3 mL)/ HNO_3 (2 mL), connect with condenser and heated at 90 °C in oil bath for an hour. Here if condenser not connected and directly acid digestion done by keeping the cap tightly closed bumping of the sample solution have been seen that could be dangerous and life threatening. Therefore, condenser found best in such case.

After the completion of this reaction, material was shifted to Teflon beaker, rinsed and left overnight at 70 °C to evaporate but temperature raised to 120 °C to get incipient dryness at the last stage. Then spin the whole content with aqua rigia with 3 mL of H_2O and kept warm for 5-10 minutes. Finally whole mixture transferred to centrifuge tube, rinsed with water marking up the volume up to 20 mL and this sample became ready to analyze for silicates and residues.

In fraction V metals mostly bound with crystals in their structure and minerals compounds including sediments have been identified. To remove error and background correction, blank samples were also analyzed. Quality check for the instrument was performed by observing absorbance for every 10 samples run.

3.9 Bioavailability of REEs in Plants

3.9.1 Pre-treatment of samples

After completing field trip, the plant samples were taken to laboratory. All the collected plant samples were first cleaned with tap and distilled water in an ultrasonic water bath to remove dirt, mud or any adhering particles and then with Milli-Q water. Samples were air dried for three months and then all parts of each plant (root, shoot,

leaves, and flower) were separated, grind, weighted and stored in clean plastic bags separately.

3.9.2 Sample preparation and analysis

After drying each part of the sample were separated including leaves, shoots, roots and some of them containing flowers. Then they were grinded to obtain homogeneous particle size and sieved. After that 0.1 g of each sample weighted and digested in microwave digester as shown in **Figure 3.9 (a)** using 7 HNO_3 and 2 mL H_2O_2 with power time system for 20 minutes. Samples were triplicate to get better results. To get reliable results, standard reference materials (Spinach leaves- SRM 1570a) and (Apple leaves-1515a) were run together with samples. After digestion samples were diluted to 50 mL and then analyzed by ICP-MS as shown in **Figure 3.9 (b).** All the samples were digested and analyzed for REEs.

(a) (b)

Figure 3.9: (a) Microwave digester (Titan- MPS, USA) (b) ICP-MS (7500ce-Agilent) used in bioavailability analysis.

3.9.3 Translocation factor (TF)

Translocation factor for REEs in plants was described as a ratio of REEs in a plant shoot in that in plant root given in Equation 3.5 (Mohebbi et al., 2012).

$$TF = C_{shoot} / C_{root} \quad \text{(Equation 3.5)}$$

Where C_{shoot} and C_{root} present the concentrations ($\mu g\ g^{-1}$) of REEs in the shoot and root of the plant, respectively. TF >1 represent that translocation of metals effectively from the root to the shoot and accumulator or hyperaccumulator species of plant while with TF < 1 nominated as tolerant (Zhang et al., 2002, Fayiga & Ma, 2006).

3.9.4 Bioconcentration Factor (BCF)

Bioconcentration factor (BCF) was calculated for all REEs in plant species by using the following Equation 3.6 (Malik et al., 2010, Zayed et al., 1998).

$$BCF = C_{leaves} / C_{soil} \quad \text{(Equation 3.6)}$$

Where C_{leaves} and C_{soil} presents the concentrations of REEs in the leaves ($mg\ kg^{-1}$) and soil of plant ($mg\ kg^{-1}$), respectively.

3.9.5 Bioaccumulation Factor (BAF)

For the determination of REEs in plant species, bioaccumulation factor (BAF) was calculated using following Equation 3.7. Plants having BCF and BAF > 1 are considered as hyperaccumulator and accumulators while BCF and BAF < 1 is termed as tolerant (Cluis, 2004).

$$BAF = C_{plant} / C_{soil} \quad \text{(Equation 3.7)}$$

Where C_{plant} and C_{soil} presents the concentrations of REEs in the stem ($mg\ kg^{-1}$) and root of plant ($mg\ kg^{-1}$), respectively.

3.10 Environmental impact assessment in soil and sediments

Degree of pollution in sediments and soil was calculated by using different environmental parameters by computing Microsoft excel 2013.

3.10.1 Enrichment factor (EF) and geoaccumulation index (Igeo)

Enrichment factors for the sediment and soil was calculated by using Equation 3.8 given Buat-Menard and Chesselet (Buat-Menard & Chesselet, 1979).

$$EF = \left(\frac{M}{R}\right) sample \Big/ \left(\frac{M}{R}\right) UCC \qquad \text{(Equation 3.8)}$$

M = concentration of the element, R = concentration of Reference Element. (M/R)UCC being ratio in continental crust. Sediment samples were found with 0.57 to 5.28 standard deviation. Classification for enrichment factor is given in seven classes (Appendix A). Igeo is calculated by using Equation 3.9 given by (Muller, 1969) as:

$$I\ geo = log2\ (\frac{Cn}{1.5} * Bn) \qquad \text{(Equation 3.9)}$$

Cn = metal (n) concentration in sediment, Bn = background value of metal (n), 1.5= correction factor (matrix correction).

3.10.2 Contamination evaluation (CF and PLI)

Sediment/soil pollution was also evaluated by using different factors such as CF and PLI. Contamination factor (CF) is classified into four classes by (Hakanson, 1980) as shown in **Equation 3.10.**

$$CF = M\ sample \Big/ M\ background \qquad \textbf{(}\text{Equation 3.10)}$$

Pollution load index (PLI) was also calculated for all sediment samples collected and analyzed given by (Tomlinson et al., 1980) as shown in **Equation 3.11**.

$$PLI = (CF1 \times CF2\ \times CF3\ \times CF4\ \times \ldots\ldots \times CFn)1/n \qquad \text{(Equation 3.11)}$$

3.11 Quality Control (QC) and Quality Assurance (QA)

Quality control (QC) and quality assurance (QA) was maintained throughout the field and laboratory work. For *In situ* measurements, instruments used were pre-calibrated using standards. In the field for water samples, QA was also maintained by every time

washing and drying the instruments, wearing gloves, carful sample collection, taking measurements, acidifying and preserving in the cooling boxes immediately.

In laboratory work, standard reference material was used to verify the data obtained in the analysis. Water quality analysis was done for REEs using SRM 1643e. The results are shown in **Table 3.1.** Table represents the recovery of the elements in the SRM, limit of detection (LOD), limit of quantification (LOQ) and coefficient of variation (CV %). The data shows promising in certified and obtained values and recovery is also satisfactory.

Quality control (QC) and quality assurance (QA) of the method used in sediment analysis was done by using SRM-4354. The results are shown in **Table 3.2**. Good recovery rates and low limit of detection confirms the validity of the method applied. Recoveries were found from 87.1 to 99.7 %. Limits of detection were below 0.1 which represents accuracy among the data.

For the soil analysis, QC and QA was performed by simultaneous analysis of the blank and certified reference material for soil. Promising results between analyzed and certified concentrations were obtained for all measured elements. The precisions of the measurements were shown as the percentage recovery. The results exhibited reasonably good precisions for all studied elements and typical recovery for rare earth elements with 2586 for all reference samples. The results for SRM with their recoveries are shown in **Table 3.3.**

Plant parts were analyzed using microwave acid digestion method. QA and QC in the results was maintained using two standard reference materials (SRMs). SRM of spinach leaves (1570) and apple leaves (1515a) were analyzed in the same way as the samples. The data was calculated in terms of recovery, limit of detection, limit of quantification

and coefficient of variation which shows reliability in the results. Results are expressed in **Table 3.4**.

3.12 Statistical data analysis

Statistical data analysis was carried out on the data obtained from various physical and chemical analysis. Descriptive statistics and chemometric tools have been used to analyze the data obtained in this research. In order to analyze, data pre-treatment was carried out. It has been noted that data pre-treatment is essential, especially standardization and normalization because without normalization, elements with higher concentration will have more influence compared to low level concentration elements (Li et al., 2014).

3.12.1 Principal Component Analysis (PCA)

PCA is one of the unsupervised linear multivariate data reduction methods which is used for variable reduction and is based on the correlations between the variables (Brereton, 2003). PCA maps samples into new uncorrelated latent variables named principal components (PCs) (Granato et al., 2010). From the PCs two or three dimensional score plots can be drawn with loadings presented as vectors (Zhang et al., 2013).

3.12.2 Factor Analysis (FA)

Factorial analysis is an explorative analysis similar to cluster analysis that describes observed variables in terms of unobserved latent factors which are represented as linear combination of the observed variables. Factorial analysis reduces the number of variables by reducing the dimensions of the observations and helps in providing meaningful explanation of the observed variables via the latent factors. The key concept of factorial analysis is that the observed variables have similar paterrens of the response because they are all in relation with a latent variable (the latent factor) (Sall et al., 2012).

Table 3.1: Recovery (%), limit of detection (LOD) and limit of quantification (LOQ) for the SRM 1643e.

SRM(1643e)		Certified values	Obtained values	Recovery	LOD	LOQ
No. of samples	Elements	(µg L^{-1})	(µg L^{-1})	%	(µg L^{-1})	(µg L^{-1})
1	Al	141.8 ± 8.6	140.5 ± 9.5	99	0.033	0.11
2	As	60.45 ± 0.72	59.78 ± 0.88	98.8	0.008	0.02
3	Ba	544.2 ± 5.8	542.2± 6.76	99.6	0.091	0.3
4	Be	13.98 ± 0.17	13.21 ± 0.23	94.4	0.072	0.24
5	Cd	6.568 ± 0.073	6.112 ± 0.12	93	0.055	0.18
6	Co	27.06 ± 0.32	27.01 ± 0.54	99.8	0.012	0.04
7	Cu	22.76 ± 0.31	21.96 ± 0.45	96.4	0.077	0.25
8	Fe	98.1 ± 1.4	97.4 ± 1.87	99.2	0.043	0.14
9	Li	17.4 ± 1.7	17.26 ± 1.66	99.1	0.078	0.26
10	Zn	78.5 ± 2.2	78.3 ± 3.2	99.7	0.011	0.03
11	Cr	20.4 ± 0.24	20.1 ± 0.37	98.5	0.003	0.01
12	Ni	62.41 ± 0.69	62.14 ± 0.95	99.5	0.063	0.21

Table 3.2: SRM 4354 for sediment analysis with recovery (%), limit of detection (LOD) and limit of quantification (LOQ).

SRM(4354)		Certified values	Obtained values	Recovery	LOD	LOQ
No. of samples	Elements	(mg kg^{-1})	(mg kg^{-1})	%	(µg L^{-1})	(µg L^{-1})
1	Sc	7.2[a]	6.85 ± 0.01[b]	95.1	0.075	0.25
2	Y	26[a]	25.1 ± 0.04[b]	96.5	0.038	0.12
3	La	93[a]	92.8 ± 0.24[b]	99.7	0.042	0.14
4	Ce	153[a]	151.9 ± 0.11[b]	99.2	0.0055	0.018
5	Pr	67[a]	65.4 ± 0.04[b]	97.6	0.069	0.23
6	Nd	150[a]	148.9 ± 0.06[b]	99.2	0.001	0.003
7	Eu	2.8[a]	2.62 ± 0.10[b]	93.5	0.0089	0.02
8	Gd	14[a]	13.33 ± 0.07[b]	95.2	0.076	0.25
9	Tb	31[a]	27.8 ± 0.03[b]	89.6	0.017	0.056
10	Dy	21[a]	20.6 ± 0.11[b]	98	0.066	0.22
11	Ho	6.7[a]	6.11 ± 0.14[b]	91.1	0.028	0.093
12	Er	9.5[a]	8.78 ± 0.02[b]	92.4	0.096	0.32
13	Tm	4.5[a]	4.44 ± 0.05[b]	98.6	0.015	0.05
14	Yb	3.7[a]	3.62 ± 0.01[b]	97.8	0.012	0.04
15	Lu	14[a]	12.2 ± 0.11[b]	87.1	0.082	0.27

* a The certified values are calculated from a single method or a mean of two method
b All the obtained values are based on three observations and reported as mean ± SD

Table 3.3: Standard reference material (SRM-2586) for the soil with recovery (%), LOD and LOQ.

Elements	Certified (mg kg^{-1})	Obtained (mg kg^{-1})	Recovery (%)	LOD (µg L^{-1})	LOQ (µg L^{-1})
Sc	24[a]	24.6 ± 12.8 [c]	95.83	0.040	0.130
Y	21 [a]	22 ± 9.5 [c]	97.62	0.0004	0.001
La	29.7 ± 4.8[b]	29 ± 5.1 [c]	97.64	0.0004	0.002
Ce	58 ± 8 [b]	56 ± 9.5 [c]	96.55	0.002	0.005
Pr	7.3 [a]	7.01 ± 2.3 [c]	97.26	0.001	0.004
Nd	26.4 ± 2.9 [b]	26 ± 3.1 [c]	98.48	0.001	0.002
Eu	1.5 [a]	1.58 ± 0.7 [c]	96.67	0.001	0.003
Gd	5.8 [a]	6.03 ± 2.9 [c]	99.13	0.002	0.007
Tb	0.9 [a]	1.1 ± 0.28 [c]	94	0.001	0.002
Dy	5.4 [a]	5.3 ± 1.2 [c]	98	0.001	0.002
Ho	1.1 [a]	1.0 ± 0.062 [c]	91	0.0003	0.001
Er	3.3 [a]	3.7 ± 0.25 [c]	93.94	0.001	0.003
Tm	0.5 [a]	0.5 ± 0.07 [c]	100	0.0002	0.001
Yb	2.64 ± 0.51[b]	2.62 ± 0.73 [c]	96	0.006	0.019

*[a] The certified values are calculated from a single method or a mean of two method

[b] The certified values are calculated based in two or more analysis and reported as mean ± SD

[c] All the obtained values are based on three observations and reported as mean ± SD

Table 3.4: Summary of elements with their recoveries (%), limit of detection (LOD), limit of quantification (LOQ) in certified reference materials for apple leaves (1515a) and spinach leaves (1570a).

S/NO.	Elements	SRM 1515a reference conc. (µg/g)	SRM 1515a measured conc. (µg/g)	Recovery (%)	LOD (µg/L)	LOQ (µg/L)	CV (%)
1	Cd	0.013[a]	0.012 ± 0.001[c]	92.3	0.029	0.09	0.08
2	Gd	3[a]	2.8± 0.25[c]	93.3	0.0069	0.023	0.08
3	La	20[a]	18.9 ± 0.45[c]	94.5	0.0031	0.01	0.02
4	Ba	49[a]	46.8± 2.9[c]	95.5	0.051	0.17	0.06
5	B	27[a]	26.2± 1.9[c]	97	0.088	0.29	0.07
6	Ce	3[a]	2.88± 0.41[c]	96	0.0011	0.0036	0.14
7	Eu	0.2[a]	0.19± 0.004[c]	95	0.0036	0.012	0.021
8	Nd	17[a]	16.1 ± 1.8[c]	94.7	0.01	0.033	0.11
9	Yb	0.3[a]	0.27± 0.01[c]	90	0.01	0.033	0.03
10	Sc	0.03[a]	0.028± 0.001[c]	93.3	0.103	0.34	0.03
S/NO.	**Elements**	**SRM 1570a reference conc. (µg/g)**	**SRM 1570a measured conc. (µg/g)**	**Recovery (%)**	**LOD (µg/L)**	**LOQ (µg/L)**	**CV (%)**
1	Al	310 ± 15[b]	287 ± 11.5[c]	92.5	0.145	0.48	0.04
2	As	0.068 ± 0.012[b]	0.056± 0.008[c]	82.3	0.341	1.13	0.14
3	Ni	2.142 ± 0.058[b]	2.118± 0.056[c]	98.8	0.0059	0.019	0.02
4	Eu	0.0055 ± 0.0010[b]	0.0048± 0.0011[c]	87.2	0.0015	0.005	0.22
5	Sc	0.0055 ± 0.0006[b]	0.0051± 0.0095[c]	92.7	0.0063	0.021	1.86
6	Cu	12.22 ± 0.86[b]	12.23± 0.84[c]	100	0.0781	0.26	0.068
7	Co	0.393 ± 0.030[b]	0.382 ± 0.022[c]	97.2	0.003	0.01	0.057

3.12.3 Hierarchical Culture Analysis (HCA)

Hierarchical Culture analysis (HCA) is carried out to find the cluster of samples. It is also named as agglomerative clustering. HCA basically acts like a cluster which starts at its own row resulting in calculating distance and grouping the clusters closer to each other. Such clusters continue to make a single cluster at the end. There are five rules for determining the distance between clusters, they are the centroid, complete, average, ward and single. However, Wards method was used in this research to find the clustering in soil samples.

Summary

The current chapter detail out the methodology adopted in this research. Instruments used in the study have been given. Sampling locations map in the study area has been defined. Pre-sampling, sampling, preservation followed by laboratory analysis has been elaborated in detail. Analysis and physico-chemical parameter for water, sediments, soil and plants have been described. Different environmental impact assessment factors have been quoted in the equations. Quality control (QC) and quality assurance (QA) maintained throughout the research (*In situ* and laboratory) has also been explained. Statistical data analysis using PCA, FA and HCA has been also explained.

CHAPTER 4: ANALYSIS OF WATER, SEDIMENT AND SOIL

4.1 Water Analysis

Rare earth elements (REEs) have become a major concern these days especially in mining and industrial countries due to their persistent toxicity, radioactive nature and accumulation. Water is considered as most important, abundant and useful natural resource on the earth essential for sustaining life (Prasoon et al., 2015).

In this study thirty water samples were taken from mining lakes, ponds and Kinta River. Water samples were collected from 2014-2015 in two times field works. QC and QA was maintained throughout the fieldwork by using gloves, safety jackets, using precalibrated instruments, repeated washing of probes for every instrument, acidifying the samples and immediately preserving in cooling boxes.

4.1.1 Physico-chemical parameters

Table 4.1 represents the physico-chemical characteristics of mining lake water and Kinta River. Use of water supply for portable, agriculture or as raw water is based on the criteria set by Interim National Water Quality Standards Malaysia (2006) and Environmental Quality Report (2006) as shown in **Table 4.2** and **Table 4.3.**

Table 4.1: Physico-chemical characteristics of ex-tin mining lake for 20 samples and Kinta River water for 10 samples.

Parameter	Temp	Salinity	TDS	pH	SPc	ORP	DO	DO	Fluoride	Chloride	Bromide	Nitrites	Nitrates	TSS	Sulphate	Ammonia
Units	° ℃	NTU	mg L^{-1}	pH	µS/cm	mV	mg L^{-1}	% age	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}	mg L^{-1}
Mining Lake water																
Average	31.80	0.15	1190.52	8.3	2194.09	387.73	12.79	189.50	0.80	3.52	0.56	1.52	115.50	127.60	43.32	0.54
Min	29.50	0.06	1179.80	6.7	2134.00	328.00	8.10	133.00	0.30	2.11	0.08	0.35	62.02	65.00	38.60	0.17
Max	34.50	0.19	1199.50	8.9	2237.50	488.00	22.50	325.00	1.17	5.61	1.20	2.42	151.90	208.00	46.31	1.20
Median	31.80	0.15	1191.90	8.7	2221.05	372.50	10.60	153.50	0.80	2.93	0.47	1.66	118.05	121.00	43.62	0.53
Stdev.	1.33	0.03	6.19	0.7	41.58	42.17	5.04	71.64	0.25	1.13	0.30	0.65	28.99	50.12	2.03	0.27
Range	5.00	0.13	19.70	2.2	103.50	160.00	14.40	192.00	0.87	3.50	1.12	2.07	89.88	143.00	7.71	1.03
Kinta River water																
Average	29.05	0.13	1802.37	6.4	2038.95	444.20	17.69	388.20	1.12	4.42	0.53	2.17	103.20	196.50	69.22	136.63
Min	27.60	0.07	1779.50	5.7	2002.80	392.00	11.50	163.00	0.88	2.15	0.38	0.97	64.21	102.00	55.59	0.75
Max	29.70	0.15	1892.90	6.8	2203.20	498.00	21.20	1050.00	1.47	5.61	0.70	3.02	143.22	282.00	85.22	364.00
Median	29.25	0.14	1794.45	6.5	58.42	445.00	18.85	305.50	1.03	4.66	0.53	2.24	104.00	202.00	69.19	1.38
Stdev.	0.64	0.03	3.23	0.4	5.84	3.82	3.36	2.63	0.21	1.10	0.09	0.75	2.86	5.61	9.87	1.75
Range	2.10	0.08	113.40	1.1	200.40	106.00	9.70	887.00	0.59	3.46	0.32	2.04	79.01	180.00	29.63	363.25

Table 4.2: Maximum allowable limit for raw water and portable water set by different Malaysian authority and USEPA.

Serial No.	Parameter	Raw untreated water (after Ministry of Health, Malaysia	Portable Water	
			Ministry of Health, Malaysia (2009)	US Environmental Protection Agency (2008) & World Health organization (2009)
1		Physical Characteristics		
	Turbidity	1000NTU	5 NTU	5 NTU
	Colour	300 Hazen	15 Hazen	5 Hazen
	pH	5.5-9.0	6.5-9.0	6.8-9.2
2		Inorganic		
	Dissolved Solids (mg L^{-1})	1500	100	500
	Total Solids	-	-	1500
	Chlorides(mg L^{-1})	250	250	250
	Nitrate (mg L^{-1})	10	10	45
	Iron Fe (mg L^{-1})	1.0	0.3	0.3
	Fluoride (mg L^{-1})	1.5	0.9	1.5
	Ammonia N (mg L^{-1})	0.5	0.5	-
	Total Nitrogen NO_3 (mg L^{-1})	1.0	-	-
	Hardness	500	500	-
	Sulphate (mg L^{-1})	400	400	400
3		Elements/Compounds		
	Mercury (mg L^{-1})	0.001	0.001	0.002
	Cadmium (mg L^{-1})	0.005	0.005	0.01
	Selenium (mg L^{-1})	0.01	0.01	0.01
	Arsenic (mg L^{-1})	0.05	0.05	0.05
	Cyanide (mg L^{-1})	0.1	0.1	0.05
	Lead (mg L^{-1})	0.1	0.05	0.05
	Chromium (mg L^{-1})	0.05	0.05	0.05
	Silver (mg L^{-1})	0.05	0.05	0.05
	Copper (mg L^{-1})	1.0	1.0	1.0
	Magnesium (mg L^{-1})	150	150	-
	Manganese (mg L^{-1})	0.2	0.1	0.05
	Zinc (mg L^{-1})	5.0	5.0	5.0
	Sodium (mg L^{-1})	200	200	200
	Aluminium (mg L^{-1})	-	0.2	0.2
	Oil & Grease (mg L^{-1})	0.3	0.3	0.3
	Phenol (mg L^{-1})	0.002	0.002	-

Table 4.3: Interim National Water Quality Standards for Malaysia (INWQS), (2006).

Parameters	Unit	Classes					
		I	IIA	IIB	III	IV	V
Ammonical Nitrogen	mg/l	0.1	0.3	0.3	0.9	2.7	> 2.7
BOD	mg/l	1	3	3	6	12	> 12
COD	mg/l	10	25	25	50	100	> 100
DO	mg/l	7	5-7	5-7	3-5	< 3	< 1
pH	-	6.5-8.5	6.5-9.0	6.5-9.0	5-9	5-9	-
Color	TUC	15	150	150	-	-	-
Elec. Conductivity	µS/cm	1000	1000		-	6000	-
Floatables	-	NV	NV	NV	-		-
Salinity	%	0.5	1		-	2	-
Taste	-	NOT	NOT	NOT	-		-
Total suspended solids	mg/l	25	50	50	150	300	300
Temperature	° C		Normal + 2 °C		Normal + 2°C	-	-
Turbidity	NTU	5	50	50	-	-	-
Fecal Coliform	counts/100ml	10	100	400	5000 (20000)	5000 (20000)	-
Total Coliform	counts/100ml	100	5000	5000	50000	50000	>50000

Note: Class Uses

Class I: Conservation of natural environment.

Water Supply 1 – practically no treatment necessary.

Fishery 1 – very sensitive aquatic species.

Class IIA: Water Supply II – conventional treatment required.

Fishery II – sensitive aquatic species.

Class IIB: Recreational use with body contact.

Class III: Water Supply III – extensive treatment required.

Fishery III – common, of economic value and tolerant species; livestock drinking.

Class IV: Irrigation.

Class V: None of the above.

Detail of each parameter studied for water samples is explained by using box and whisker plots as follows:

4.1.1.1 Temperature

Temperature ranged from 29.5-34.5 °C and 27.6-29.7 °C for ex-tin mining lake and river water samples respectively as shown in **Figure 4.1 (a)**. Small changes in temperature of water have been seen at different locations along the lake. Due to tropical lowlands and heavy rainfall with high sunshine such temperature is considered normal for the current study area.

4.1.1.2 Salinity

Salinity was observed with nearly same value of 0.145 % in all the water samples collected and analyzed from lake and river. There were not so variations in this parameter.

4.1.1.3 pH

Water in the lake found nearly neutral in nature as shown in **Figure 4.1 (b**). pH for mining lake water samples varies from acidic to basic while for river water was found acidic to neutral (5.7-6.8) with high pH 6.8 at sampling location R-8. Lake water draining to the nearby areas is more basic (6.7-8.9) than water chief inflow to the lake. Neutral pH may be because of transformation of mining land into oil palm plantation, formation of wetlands and dilution effects caused by rainfall and water flow channel.

4.1.1.4 Dissolved Oxygen (DO)

All the water samples were found high in DO as shown in **Figure 4.1 (c)**. For lake water samples studied average DO was found 12.79 mg L^{-1} whereas for river water samples it was found 17.69 mg L^{-1}. The highest DO was found at five locations in lake waters (LI, L2, L3, L5 and L6) with more than 19 mg L^{-1}. Both values were higher than allowable limits. DO is mostly affected by temperature. Increase in temperature decreases the solubility of oxygen in water. However, in study area DO was found higher

than the allowable limit set by national water quality agencies. High sunshine and heavy rainfall could be the factors responsible for high DO levels in water.

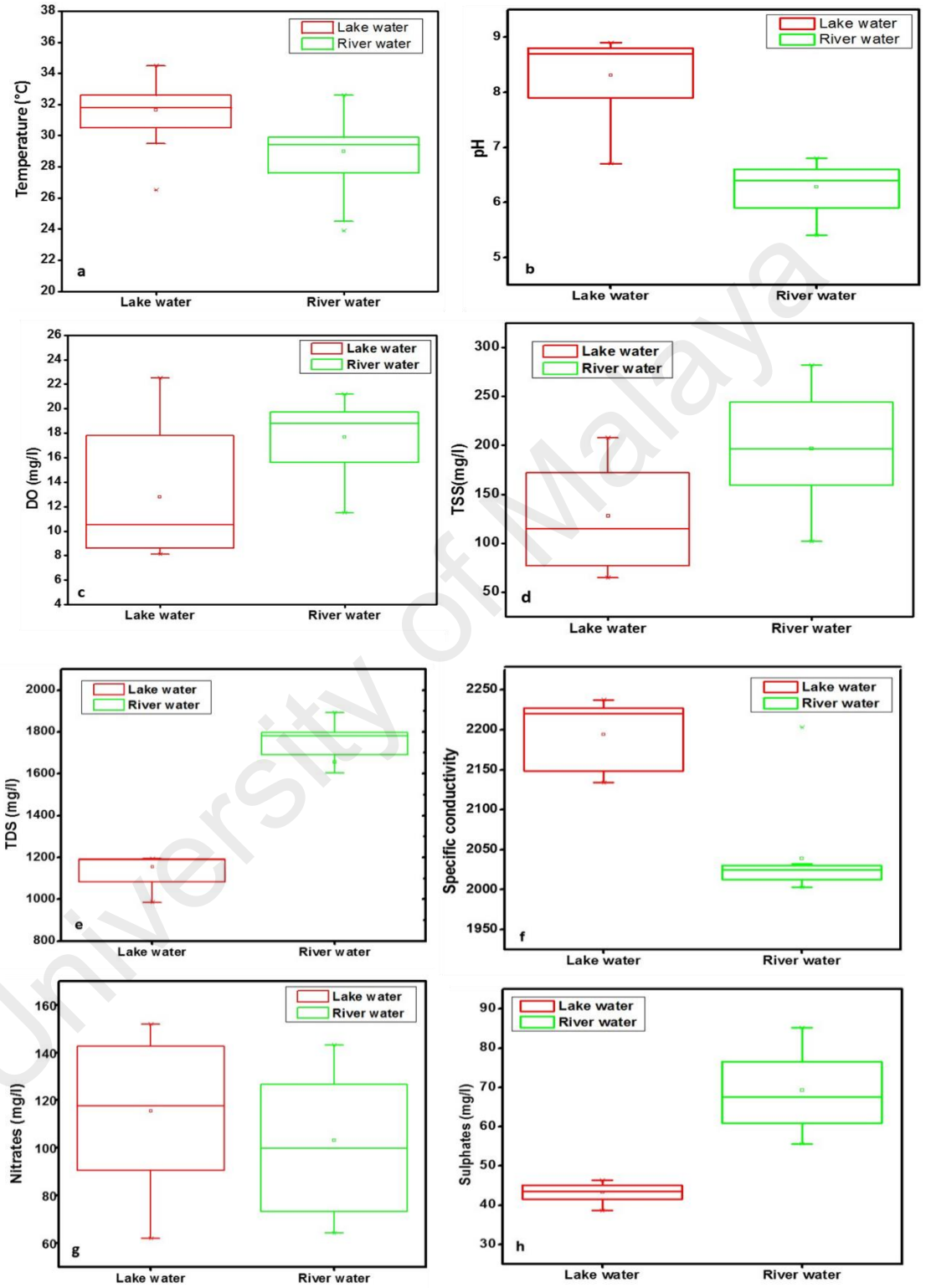


Figure 4.1: Box and whisker plots showing physical parameters of water quality for lake and river water quality (a) Temperature (b) pH (c) DO (d) TSS (e) TDS (f) Specific conductivity (g) Nitrates (h) Sulphates.

4.1.1.5 Total suspended solids (TSS)

In the study area TSS was also found higher. In lake water average TSS were 127.60 mg L^{-1} and in Kinta river water were 196. 50 mg L^{-1} as shown in **Figure 4.1 (d)**. River water was found with higher TSS than lake water. River water flows throughout the length of the study area and receives water from different areas. In both water bodies TSS were high compared to the interim national water quality allowable standards. During wet season (rainy season) TSS slightly increase in concentration compared to dry season due to increased precipitation, soil and solid particles from urban and agricultural runoff.

4.1.1.6 Total dissolved Solids (TDS)

TDS in the study area has been found high having an average value of 1190 mg L^{-1} for lake water samples and 2038.95 mg L^{-1} for river water samples as shown in **Figure 4.1 (e)**. Lake water has less average amount of TDS than allowable limit as given in **Table 4.3** while the river water shows much contamination having higher TDS values for all samples.

4.1.1.7 Specific conductivity (SPc)

Specific conductivity values for lake and river water samples ranged more than 2000 µs, two times greater than standard allowable limit i-e 1000 µs according to INWQS, 2006. High specific conductivity represents the higher amount of free ions in both the samples as shown in the **Figure 4.1 (f)**. Oxidation reduction potential varies from 328-488 Mv. Maximum value is shown at sampling station L-17.

4.1.1.8 Nitrates (NO_3^-)

Nitrates were also analyzed for mining lake water and river water samples as shown in **Figure 4.1 (g)**. The results indicate ex tin mining lake water with high nitrites and nitrates (Muhammad et al., 2012). Average nitrates in ex-mining lake water were 115.50

mg L^{-1} and in river water were103.20 mg L^{-1}. Both water bodies show higher values compared to allowable limits.

4.1.1.9 Sulphates (SO_4^{2-})

Sulphates in river waters were significantly high than INWQS Malaysia and WHO allowable limits. Average amounts of sulphates in ex tin-mining lake and Kinta River were 43.32 mg L^{-1} and 69.22 mg L^{-1} respectively as shown in **Figure 4.1 (h)**. Sulphide bearing bedrocks around the upper part of the ex-mining lake gets oxidized when exposed to air or water resulting in sulphide mineral oxidation. Production of iron oxides and sulphuric acid that affects the quality of water, decreasing pH and making it unsuitable for aquatic life. Other factors may be industrialization, agriculture, aqua culture, and construction and mining activities. These results support the previous study of Azyana and Nik. (2012) and Akif et al. (2014). Sulphates were below the allowable standard limit.

4.1.1.10 Ammonium (NH_4^+)

Water samples from study area also contain ammonium ions. Lake water contain 0.54 mg L^{-1} whereas river water contain at some locations 136.60 mg L^{-1} average concentration as described in **Table 4.1**. High amount of ammonium ions in river water indicate higher organic components dissolved. It is said that river water is more polluted because it receives water from industries, agriculture, commercial waste etc.

4.1.1.11 Chlorides (Cl^-)

Chlorides in lake and river water from the studied area were found with lower concentration of chlorides in both water bodies than allowable national limit for raw and portable water **(Table 4.3)**.

Other anions such as bromides, nitrites, fluorides were also detected in safe amount in lake and river water samples from the study area. Based on the current findings mining

lake water could be categorized into class IV and V according to INWQS. Such water is used for plantation and also by the residents of nearby area circulating these rare earths throughout the food chain (Al-Fugara et al., 2014, Rahmanian et al., 2015).

4.1.2 REEs in ex-tin mining lake waters and Kinta River

Based on SRM results and recovery of the samples, the concentration of REEs in water from ex mining lake and Kinta River was found. **Table 4.4** and **Figure 4.2** represents average concentration of REEs in study area. Analytical data is provided in **Appendix B.**

Cerium was found in the highest concentration from 45.2-49.08 µg L^{-1} with average value 46.5 µg L^{-1}. Ce is the major trace element in lanthanide series and chiefly found in REE bearing mineral. Maximum amount was found at sampling location L-13 (49.08 µg L^{-1}). This site was located near the uphill of the mining lake and due to heavy rainfall and weathering process, Ce is leaching into lake water at very high rate. Yb was found in higher amount at location 20 with 23.11 µg L^{-1}.

Lanthanum, yttrium and scandium were higher at L-16 with 20.54, 17.96 and 9.66 µg L^{-1}, respectively representing this lake point more concentrated with monazite minerals or complexes. At site L-20 Er, Nd and Pr were chiefly found in 13.75, 12.68 and 10.67 µg L^{-1}. Here distribution of REEs found much uniform. Gd and Ho were in lower concentration but their maximum amount was found at L-17 (7.99 and 4.55 µg L^{-1}).

Table 4.4: Average concentration (µg L^{-1}) of REEs in ex-tin mining lake (20 samples) and river water (10 samples) with light and heavy rare earth elements.

Elements	Sc	Y	La	Ce	Pr	Nd	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	Light rare earth elements(LREES)							Heavy rare earth elements (HREES)							
Mining Lake water															
Average	16.71	13.12	17.77	46.50	8.96	10.75	3.03	6.83	2.42	12.08	3.80	12.74	15.55	18.23	3.72
Min	7.85	10.09	16.15	45.20	8.30	9.41	2.71	6.11	2.01	11.14	3.17	12.05	14.35	15.36	2.88
Max	175.47	17.98	20.54	49.08	10.67	12.91	3.88	7.99	3.74	13.41	4.58	13.57	16.88	23.11	4.25
Median	9.13	10.72	16.63	45.39	8.42	9.66	2.86	6.22	2.12	11.74	3.56	12.44	14.97	17.71	3.79
Std.dev.	0.72	3.46	1.64	1.43	0.92	1.44	0.32	0.80	0.48	0.71	0.55	0.55	0.94	2.70	0.37
Range	167.62	7.89	4.39	3.88	2.37	3.50	1.17	1.88	1.73	2.27	1.41	1.52	2.53	7.75	1.37
Sum of conc.	175.47	262.37	355.47	930.05	179.22	214.93	60.57	136.51	48.31	241.55	75.95	254.79	310.99	364.648	74.31
ΣLREE	2178.08														
ΣHREE	1507.06														
ΣREE	3685.14														
Kinta River water															
Average	9.87	7.37	11.51	29.95	7.74	9.23	1.72	5.29	1.75	7.63	1.33	8.49	10.50	12.66	1.81
Min	4.32	6.81	11.03	28.71	7.38	9.06	1.02	5.04	1.62	7.44	1.05	8.36	10.28	12.33	0.94
Max	54.31	7.96	12.82	33.15	8.21	9.41	2.46	5.49	1.89	7.82	1.56	8.77	11.05	13.44	2.44
Median	5.32	7.34	11.34	29.38	7.67	9.22	1.68	5.34	1.75	7.60	1.29	8.44	10.47	12.55	1.84
Std.dev.	0.54	0.39	0.50	1.59	0.29	0.11	0.49	0.14	0.10	0.13	0.17	0.14	0.23	0.35	0.47
Range	49.99	1.15	1.79	4.44	0.83	0.35	1.44	0.45	0.27	0.38	0.51	0.41	0.77	1.11	1.50
Sum of conc.	54.31	73.69	115.14	299.52	77.44	92.26	17.21	52.94	17.47	76.34	13.27	84.85	104.95	126.61	18.06
ΣLREE	729.57														
ΣHREE	494.49														
ΣREE	1224.06														

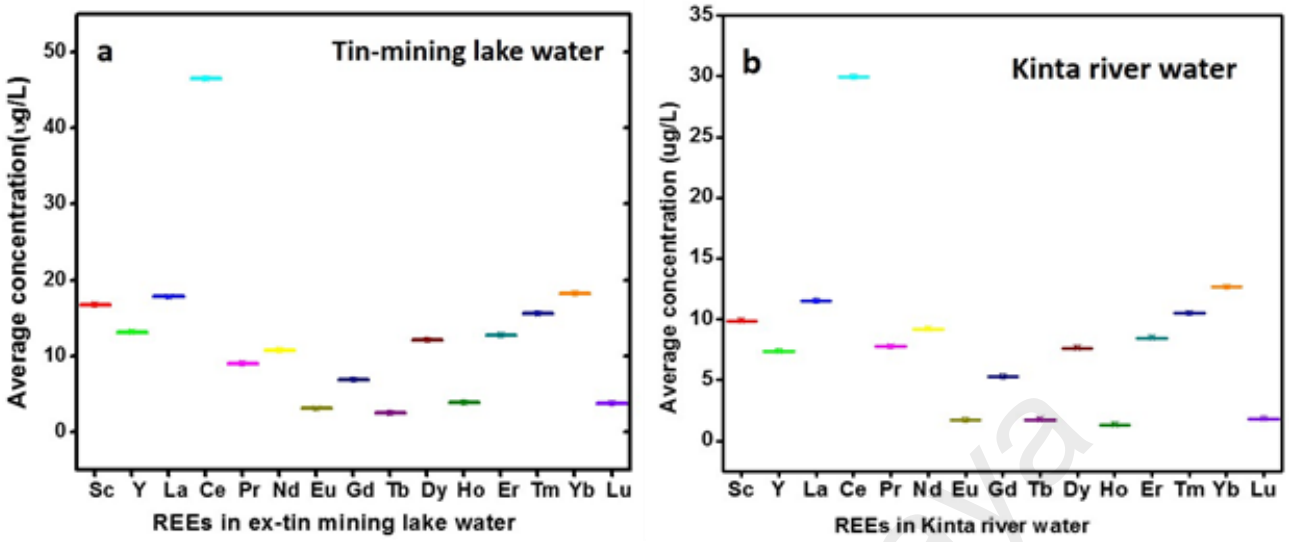


Figure 4.2: Average concentrations of REEs in ex-mining lake water and river water samples from the study area.

Previous studies indicate higher concentrations of Gd in river waters due magnetic resonance imaging technology widely applied as modern technique recently (Ogata & Terakado, 2006; Kulaksız &Bau, 2007; Hatje et al., 2016). Dy concentration was higher (13.41 µg L^{-1}) at site 15. Tb was found in less concentration but still the concentration was 3.74 µg L^{-1} at L-8. Such analysis reveal somewhat evenly distribution of REEs throughout the mining lake water.

Average REEs value found in current study are comparable with average values recorded by Muhammad et al. (2014) conducted in Bestari Jaya water samples. Acidic (pH 2.7) lake and ground water in Germany contain F^-, SO_4^{2-} and two of the REEs i-e lanthanum (La) and cerium (Ce) 70 µg L^{-1} and 160 µg L^{-1}, respectively (Bozau et al., 2004). The current study shows lake water rich in sulphates (43.32 µg L^{-1}), pH in the range neutral (7) to less basic (6) and high average La and Ce concentration of about 17.77 µg L^{-1}, 45.50 µg L^{-1} respectively. For a long time cassiterite ore, recovered from

alluvium in the plains of Kinta River and its tributaries. Tin has also been mined from lodes, veins and stock works in limestone, schist and granite. Monazite, ilmenite, zircon, and other heavy metals had also been used in tin mining industry (Ingham and Bradford, 1960). Tin tailing consist of magnetic minerals (iron ore, columbite) and non-magnetic minerals (cassiterite, monazite, zircon sand in large quantity and silica etc). Most of the tin tailings composed of inorganic oxides (Aigbodion et al., 2010).

Different mechanical and electrical industries running in the area use REEs in processing automobiles, magnets, glass etc. In river water sampling station (R-9) was significantly correlated with Ce, Pr, Dy, Eu, Lu and Ho (33.15, 8.21, 7.82, 2.46, 2.44 and 1.56 µg L^{-1}, respectively). Samples analyzed from location R-8 mostly found enriched in La, Y, Nd, and Gd while Tb, Er, Tm and Yb were present at site R-7. Presence of REEs in these location indicate that they are sourced from those industries using REEs in modern technologies.

The current study indicate total concentration of REEs in lake and river water samples equal to 3685 µg L^{-1} and 1224 µg L^{-1} respectively **(Table 4.4)**. Total concentration was also found for LREEs and HREEs as well. REEs in mining lake water ranged from 2.42 µg L^{-1} (Tb) to 46.50 µg L^{-1} (Ce) while Kinta river water contain REEs from 1.33 µg L^{-1} (Ho) to 29.95 µg L^{-1} (Ce). Water from ex-mining area found highly concentrated with light rare earth elements indicating the presence of monazite minerals in the area. Variations in all REEs concentration have been found but maximum value for all lake and river water samples obtained equal to 49.08 µg L^{-1}. The higher REEs in this study area refer to mining activities and anthropogenic origin.

4.1.3 Statistical analysis

Data was evaluated statistically using SPSS for normality test as shown in **Table 4.5**. From the table it was concluded that Shapiro-Wilk test clearly define normal distribution

of REEs having values $p > 0.05$ except Ho and Lu which are considered non-significant and abnormally distributed in water of mining area.

REEs concentration by linear correlation in the mining lake and river waters was determined by factor analysis (FA) which provide good chance to evaluate REEs in the study area. Pearson's correlation, descriptive analysis and principal component analysis (PCA) were determined using SPSS version 23. The correlation between different factors and REEs studied is shown in **Table 4.6**.

Value of 1 represents significant correlation between different parameters and REEs in sampling waters. TDS and pH show very weak correlation in waters meaning these two parameters independent of each other and together donot put significant impact both on the water quality and REEs. The presence of sulphates in water systems indicate that strong negative correlation with pH and relatively less strong with TDS at slightly basic pH.

Sulphates found freely in waters representing more cation anion exchange capacity. Scandium show negative strong correlation with TDS posing the presence of Rare earths bearing minerals in the abundant mined area. Yttrium show strong negative correlation with TDS in water but strong positive with Sc. Such an anomaly may refer to the monazite ores as chief source of yttrium and scandium in tin mines. This may be considered as a source of REEs and pollution hazards not only to water quality but onto public health and aquatic biota. Lanthanum is strongly positively correlated with scandium and yttrium again indicating the higher extraction of monazite mineral in the location. Lanthanum is strongly correlated in negative value with TDS in waters but good correlation found with sulphates. Cerium, praseodymium, neodymium, euphorbium, gadolinium, holmium, erbium and leutetium are strongly positive correlated with most of the REEs in mining lake waters and river waters in mining land.

Table 4.5: Skewness, kurtosis, and normality tests for rare earth elements (REEs) provided by SPSS.

Parameters	No	Mean ± SD	Mean ± SEM	Skewness	SE Skewness	Z Skewness	Kurtosis	SE Kurtosis	Z Kurtosis	Shapiro-Wilk		
										Statistic	df	Sig.
Sc	40	15.85 ± 2.30	15.85 ± 1.73	-0.491	0.427	-1.14	-1.26	0.833	-1.51	0.871	30	0.065
Y	40	29.70 ± 4.16	29.70 ± 3.93	0.74	0.427	1.73	-0.93	0.833	-1.11	0.824	30	0.05
La	40	203.2 ± 7.35	203.2 ± 3.29	0.22	0.427	0.51	-1.39	0.833	-1.66	0.863	30	0.074
Ce	40	73.83 ± 9.81	73.83 ± 6.06	-0.711	0.427	-1.66	-1.44	0.833	-1.72	0.735	30	0.058
Pr	40	17.90 ± 2.60	17.90 ± 0.95	0.185	0.427	0.43	0.41	0.833	-0.49	0.803	30	0.052
Nd	40	16.70 ± 1.80	16.70 ± 1.37	0.69	0.427	1.61	-0.84	0.833	-1	0.72	30	0.145
Eu	40	5.85 ± 0.92	5.85 ± 0.73	0.682	0.427	1.59	-0.28	0.833	-0.33	0.923	30	0.092
Gd	40	20.37 ± 1.90	5.85 ± 0.98	0.57	0.427	1.33	-0.96	0.833	-1.15	0.871	30	0.352
Tb	40	2.83 ± 0.19	2.839 ± 0.50	0.32	0.427	0.74	1.35	0.833	-1.62	0.872	30	0.692
Dy	40	30.01 ± 2.35	30.01 ± 2.12	-0.512	0.427	-1.19	-1.29	0.833	-1.54	0.803	30	0.775
Ho	40	4.60 ±0.50	4.60 ± 0.26	-0.365	0.427	-0.85	-1.36	0.833	-1.63	0.852	30	0.009
Er	40	15.54 ± 1.20	15.54 ± 1.08	-0.597	0.427	-1.39	-1.52	0.833	1.82	0.764	30	0.256
Tm	40	14.94 ± 0.46	14.94 ± 0.21	-0.46	0.427	-1.07	-1.5	0.833	-1.8	0.811	30	0.074
Yb	40	18.83 ± 0.83	18.83 ± 1.45	-0.602	0.427	-1.4	-0.55	0.833	-0.66	0.887	30	0.064
Lu	40	6.29 ± 0.90	6.29 ± 0.99	-0.732	0.427	-1.71	-0.861	0.833	-1.03	0.864	30	0.001

*SD= standard deviation, Mean concentration is given in µg L^{-1}

Such an anomaly presents anthropogenic source and the alluvium and carbonaceous rocks bearing minerals on the upper side of the lake also attribute towards geogenic source of these REEs in the mining area. REEs were extracted from tin mining's as a byproduct from REE bearing minerals such as xenotime, monazite and stuverite.

PCA determines the individual performance of REEs in water by their distribution paterrens. Variability is explained by Eigen values and varimax rotation (about 93.76 %) for waters in mining area. These factors exhibit total variance (93.76 %) with positive loadings for La, Ce, Pr, Nd, Dy and rest of the REEs in all waters. Erbium shows maximum loading in the component. These values are compared with upper continental crust values found higher in concentration in all waters. Scree plot clearly define the two component as shown in **Figure 4.3.**

Such parameters refer to the source may be considered tin bearing minerals and compounds. Geogenic process in water do not correspond to background values of REEs in mining area water bodies and high variations in the data obtained in this study corresponds to some external sources.

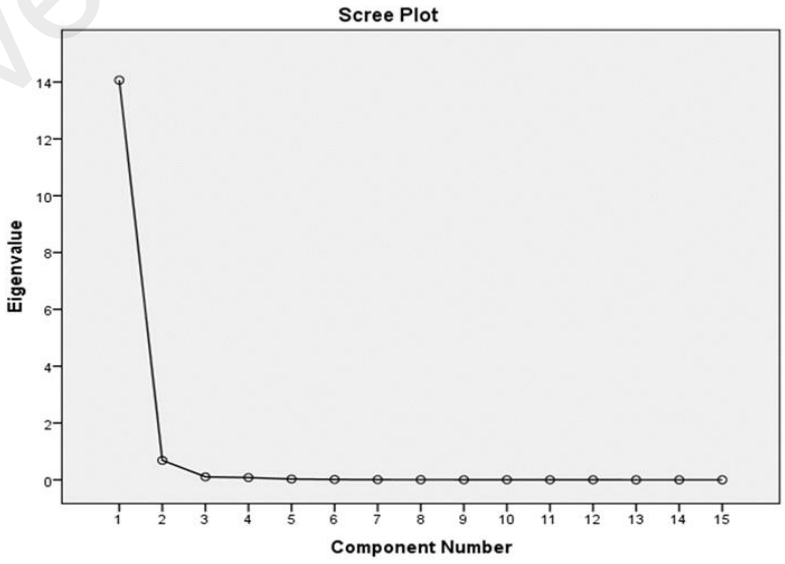


Figure 4.3: Scree plot representing two major components contributing for REEs.

Table 4.6: Correlation between different parameters for REEs in water.

	pH	TDS	SO4-	Sc	Y	La	Ce	Pr	Nd	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
pH	1	0.294	-.742**	-.521**	-.526**	-.584**	-.509**	-.561**	-.537**	-.498**	-.564**	-.351*	-.554**	0.305	-.407**	0.162	0.131	-.477**
TDS		1	-.470**	-.945**	-.945**	-.926**	-.961**	-.932**	-.936**	-.941**	-.930**	-.926**	-.941**	-.987**	-.984**	-.874**	-.918**	-.964**
SO4-			1	.673**	.694**	.732**	.664**	.727**	.692**	.651**	.714**	.583**	.702**	.535**	.595**	0.114	.329*	.649**
Sc				1	.991**	.986**	.989**	.988**	.982**	.967**	.987**	.942**	.989**	.960**	.982**	.711**	.854**	.983**
Y					1	.994**	.996**	.996**	.995**	.979**	.995**	.935**	.997**	.962**	.985**	.711**	.865**	.992**
La						1	.993**	.998**	.993**	.982**	.998**	.914**	.998**	.940**	.973**	.656**	.818**	.988**
Ce							1	.993**	.994**	.986**	.992**	.935**	.997**	.968**	.991**	.731**	.866**	.996**
Pr								1	.992**	.982**	.997**	.927**	.996**	.950**	.979**	.680**	.835**	.989**
Nd									1	.985**	.993**	.926**	.995**	.953**	.979**	.698**	.864**	.991**
Eu										1	.985**	.903**	.983**	.950**	.976**	.716**	.852**	.983**
Gd											1	.920**	.997**	.945**	.976**	.671**	.833**	.989**
Tb												1	.923**	.952**	.948**	.786**	.872**	.933**
Dy													1	.952**	.981**	.688**	.841**	.992**
Ho														1	.991**	.870**	.930**	.970**
Er															1	.808**	.905**	.991**
Tm																1	.893**	.746**
Yb																	1	.874**
Lu																		1

4.2 Sediment Analysis

4.2.1 Physico-chemical parameters of sediment from ex-mining lake

Initial physical parameters for the sediments are described in **Table 4.7**.

4.2.1.1 pH

pH for the sediment samples studied from the mining lake ranged from 5.1 to 6.8 indicating acidic to neutral nature of the sediments as shown in **Figure 4.4 (a).** Although it is simple but very important parameter in determining quality of ecosystem.

4.2.1.2 Total organic carbon (TOC)

Total organic carbon (TOC) serves as basic factor for environmental quality status in both aquatic and terrestrial ecosystem. Amount of TOC in the aquatic ecosystem is mainly associated with organic contaminants for easy access to toxicity (Avramidis et al., 2015). Total organic carbon (TOC) ranged from 4.85 ppm in SD-2 to 11.2 ppm in SD indicating the presence of organic matter in the samples given in **Figure 4.4 (b).** Such lower values show reduced risk of species organic richness in the ecosystem.

4.2.1.3 Anions (SO42-, PO43-, NO3-, NO2-) and Halides (F-, Cl-, Br-)

Sulphates were found in sediment samples ranging from 63.9- 102.4 ppm. The highest amount of sulphate was detected in sediment SD-6 as shown in **Figure 4.4 (c)**. Phosphates were detected in only two samples i.e. SD-3 and SD-4 with values 1.3 ppm and 3.7 ppm respectively. Eutrophication and lake water quality is dependent on the amount of phosphorous released from the sediments. On the other hand, nitrates were found to be the highest in concentration than any other anions in sediments. Average value of nitrates (NO_3^{-1}) was found to be 187.3 ppm **(Figure 4.4 d).** After the depletion of nitrates in anaerobic sediments, sulphates also get released to the lake water. In mining lake sediments nitrites were also detected ranging from 3.19 ppm to 7.56 ppm **(Table 4.7).**

Table 4.7: Physical parameters of the sediment samples.

Sediment parameters from ex-mining lake			(All parameters in ppm except pH)						
Sample	**pH**	**Fluorides**	**Chlorides**	**Nitrites**	**Sulphates**	**Bromides**	**Nitrates**	**phosphate**	**TOC**
SD-1	5.5	1.18	2.367	3.192	63.94	1.64	66.8	BDL	5.65
SD-2	5.1	1.31	2.285	4.319	74.84	1.35	78.9	BDL	4.85
SD-3	5.6	1.08	2.399	5.742	78.88	0.73	90.2	1.3	5.24
SD-4	5.7	1.2	3.456	6.025	88.21	0.82	148	3.7	10.8
SD-5	6.1	1.45	3.417	6.865	95.21	1.07	167	BDL	8.61
SD-6	6.3	1.264	3.486	7.13	102.58	1.15	225	BDL	8.96
SD-7	6.6	1.31	3.905	6.114	72.95	1.22	249.4	BDL	10.8
SD-8	6.8	2.34	4.347	6.991	90.31	0.99	276.8	BDL	11.2
SD-9	6.4	2.44	5.682	7.025	82.65	1.33	280.1	BDL	10.4
SD-10	6.3	2.58	5.932	7.556	96.78	1.51	291.1	BDL	10.5

Note: BDL refers to “below detection limit”

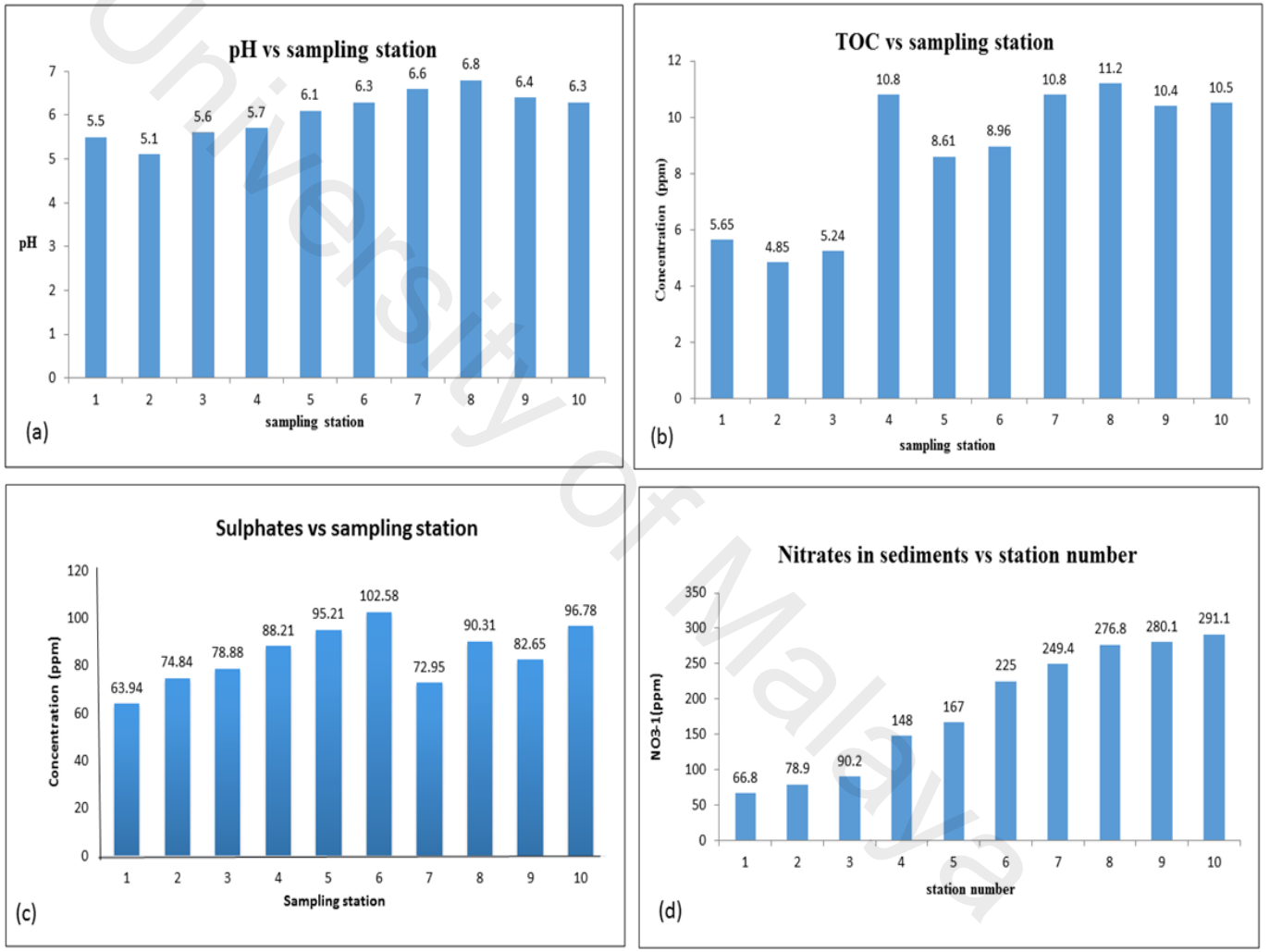


Figure 4.4: Mean concentration (mg kg^{-1}) of REEs in sediments (a) pH (b) TOC (c) Sulphates (d) Nitrates.

Fluorides in sediment samples have been found ranging from 1.08 ppm to 2.58 ppm as shown in **Table 4.7.** Chlorides were detected in 2.29 ppm to 5.53 ppm in all sediment samples as shown in **Table 4.7**. In water media concentration of chlorides vary widely. Bromides in the sediment samples were measured ranging from 0.37 ppm to 1.64 ppm. Lower concentration of bromides in the sediments reflects the high inflow water channel throughout the lake and heavy rainfall in the area caused less residence time to ions to be adsorbed on the sediment surface.

Sediments were found concentrated in most of the parameters than lake and river water samples posing greater hazard pollution source in the lake. The sedimentation rate on the upper side of the lake is higher as compared to lower ground part because of weathering process (Al-Fugara et al., 2014). This is probably due to hilly terrain and land clearing activities at the upper part of the lake. Furthermore, high rainfall throughout the year may induce erosional process around the lake.

4.2.2 REEs concentration in sediment of ex-tin mining lake

Table 4.8 and **Figure 4.5** present sediments average concentration values for the REEs from ex-mining lake. Sediment samples from 10 stations were collected and analyzed. Recovery for reference material ranged from 91.1 - 99.7 %. The values for REEs were found higher in sediments than in the lake water **(Appendix B).** La was found in maximum concentration at SD-2 with a value of 771.61 mg kg^{-1} and mean value 765.83 mg kg^{-1} in all samples. So, high degree of pollution may be related to La. Natural background value to calculate degree of pollution could not be found. Therefore, upper continental crust value was used. Average concentration of cerium in sediment was much lower (172.4 mg kg^{-1}) compared to La. Dysprosium (Dy) was found the third abundant rare element in sediment samples with average value of 88.2 mg kg^{-1}. Generally, all sediments found enriched with REEs considering as one of the biggest sources for REEs.

Very few studies have been found which focus on the REEs in the sediments while deeper water quality has been of major concern these days for the researchers (Wood, 2001). The concentration of REEs in the sediment samples from 10 stations varies from 4.21 – 771.6 mg kg^{-1}.

Slightly higher concentrations of LREEs in sediment than HREEs indicates higher transfer of REEs from lake waters to the sediment particles. Weathering of minerals from REEs bearing soil and rock could be another reason for the sediments toxicity. Here, conclusion can be made that source of REEs in the sediments is the anthropogenic activities (mining) and the rocks bearing minerals of REEs surrounding the lake. Due to weathering and erosion process and tropical region with heavy rainfall, REEs deposited on the surface of sediments make complexes with other elements and get adsorbed. Sediments are found abundant in with La, Ce, Dy, Gd, Sc, Y Nd, Pr and Eu. Mining activities in the past have left their mining waste as sediments with deposited REEs can be nominated as contaminant.

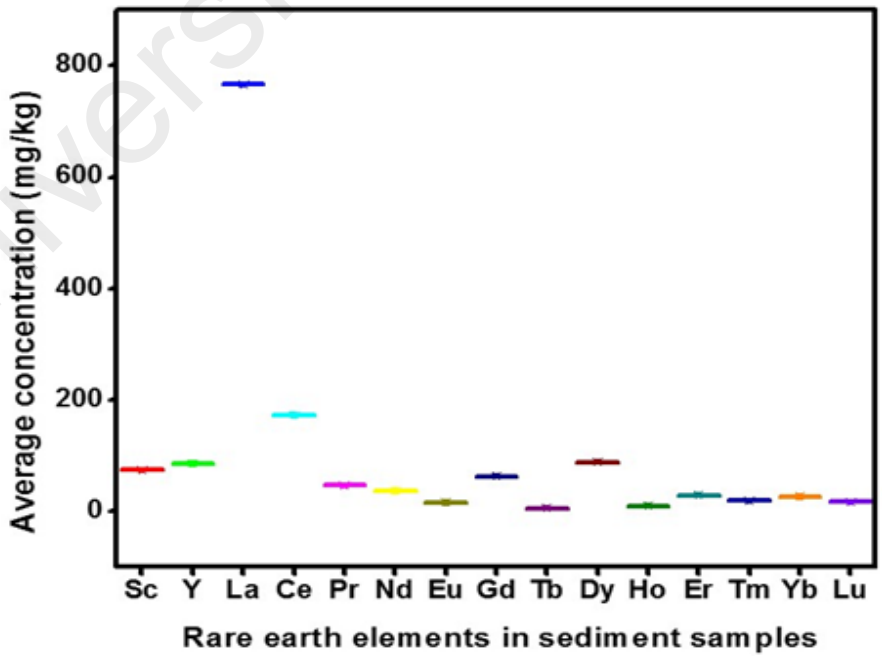


Figure 4.5: Mean concentration (mg kg^{-1}) of REEs in sediments**.**

Table 4.8: Concentration levels (µg L^{-1}) of REEs in sediment samples from ex-tin mining lake.

S.Codes	Sc	Y	La	Ce	Pr	Nd	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
SD-1	45.24±1.1	85.28±1.2	765.1±2.9	175.9±1.9	44.6±1.1	36.8±1.2	16.33±1.7	63.74±1.0	4.58±0.6	86.98±0.3	9.35±0.2	27.85±0.5	16.85±0.5	28.66±0.8	15.75±0.5
SD-2	38.12±1.0	88.76±1.2	771.61±1.6	179.55±1.5	45.2±1.0	38.69±1.0	14.25±1.3	61.08±1.1	4.71±0.08	92.28±0.30	9.3±0.2	27.2±0.3	17.61±0.3	28.17±0.4	16.29±0.2
SD-3	42.55±1.6	88.21±1.3	769.8±2.0	174.61±0.7	44.67±1.0	38.74±0.9	14.66±0.6	63.47±0.7	4.64±0.2	92.96±0.2.	9.19±0.4	28.6±0.7	17.15±0.3	27.64±0.2	16.47±0.3
SD-4	45.99±1.5	86.53±0.6	770.33±1.3	178.59±1.1	48.11±0.7	36.52±0.4	16.78±0.5	62.98±0.3	5.51±0.1	89.35±0.5	10.55±0.4	29.1±0.1	19.05±0.2	26.17±0.3	14.37±0.2
SD-5	40.65±1.0	84.11±1.5	764.59±1.1	171±1.8	50.2±1.2	37.04±0.6	15.35±0.5	62.55±0.6	5.44±0.4	84.25±0.3	10.14±0.8	29.3±0.3	18.6±0.5	25.61±0.2	16.95±0.2
SD-6	44.12±1.6	90.67±1.0	765.2±1.8	168.58±1.6	46.66±1.0	33.64±1.6	12.25±0.8	64.14±0.8	5.67±0.2	89.66±0.1	10.5±0.2	28.75±0.2	18.360.5±	24.55±0.7	15.45±0.1
SD-7	33.67±0.7	82.36±1.0	762.8±1.3	169.9±1.2	45.8±0.5	37.2±0.8	19.66±1.0	67.75±1.0	4.21±0.3	89.44±0.4	9.45±0.2	28.55±0.1	18.65±0.1	27.19±0.3	16.05±0.2
SD-8	38.52±0.9	83.47±1.4	763.55±0.8	170.8±0.4	44.23±0.4	36.88±0.3	15.65±0.6	63.77±0.6	4.54±0.4	85.27±0.8	9.92±0.2	27.51±0.6	18.6±0.1	24.5±0.1	16.55±0.2
SD-9	41.2±1.2	82.6±1.2	765.36±1.0	161.55±0.4	45.88±0.6	33.11±0.5	14.8±0.4	61.01±0.7	4.28±0.1	86.44±0.2	9.95±0.2	27.75±0.2	18.66±0.3	24.76±0.5	15.51±0.09
SD-10	34.35±1.1	80.22±1.3	760.02±1.0	173.5±0.9	44.76±0.2	35.65±0.5	15.75±0.3	54.95±0.1	4.22±0.1	86.17±0.1	9.75±0.1	27.7±0.1	18.42±0.2	24.72±0.1	15.84±0.2

Sediments collected from the hilly side show different behavior than sediments from the ground side of the ex-mining lake while sediments from the point of drainage are found less in REEs. Soil type around different parts of the lake also influenced the sediment properties. So far, no study has evaluated the source of REEs in the sediments in ex-mining lake water.

Most of sediment bound REEs were fixed on the surface and present in an inert state. Ex-mining area after evaluation for REEs was found to be rich in these elements and also detrimental effects on aquatic ecosystem. In general, decreasing trend of REEs in the sediment samples from ten stations is given as: La > Ce> Dy> Y> Gd > Pr > Sc > Nd > Yb > Er > Tm > Eu >Lu > Ho > Tb. The higher degree of pollution in the ex-mining lake is related to the sediments that acts as source of most of the REEs being deposited on the surface along with minerals.

4.2.3 Environmental Assessment

Degree of pollution in sediments is calculated by using different environmental parameters by computing Microsoft excel 2013.

4.2.3.1 Enrichment Factor (EF) and Geo-accumulation Index (Igeo)

Sediment samples were found with 0.0 to 4.6 standard deviation. Enrichment factor values with average, standard deviations, minimum, maximum, range and median are given in **Table 4.9** and **Figure 4.6.** Average EF value is maximum for Tm (124) and minimum for Nd (0.0) but generally sediments show REEs enrichment in the category minor to extremely severe enrichment (Franklin et al., 2016). Classification of samples into different categories is done on the basis of seven classes given in **Table 4.10**.

Average enrichment factor (EF) values for all REEs found as Sc (5.6), Y (0.4), La (48.5), Ce (0.4) Pr (12.7), Nd (0.0), Eu (30.7), Gd (0.1), Tb (13.4), Dy (0.4), Ho (23.2),

Er (0.2), Tm (119), Yb (0.3) and Lu (100.8). From these results it is indicated that Y, Ce, Nd, Gd, Dy, Er and Yb show no enrichment factor or minor enrichment while Sc, Pr, and Tb show moderately severe enrichment. La, Tm and Lu show extremely sever enrichment in sediment samples. Based on the classification, sediment samples fall into the category of severe enrichment. Therefore, anthropogenic contributions can be observed throughout the mining lake including the points near the catchment of water supply to the near urban area (Franklin et al., 2016).

The enrichment of surface sediments for REES in the Penang River, Malaysia indicate value less than 2 for all REEs in the samples representing less contamination of the river sediments and of natural origin (Ong et al., 2015) while this study shows much higher enrichment nearly up to 100 for Lu imposing the anthropogenic sources mainly by ore mining activities. REEs in Periube black mud show the enrichment of light REEs than High REEs. Enrichment value for light REEs observed more than 1 showing compactness of the structure whereas for the heavy REEs less than 1 showing scattered behaviour. Similar correlation was found in the study. Sediments found much deposited with LREE compared to HREE.

Geoaccumulation index (Igeo) significantly define and determine contamination level in sediments. For the first time Muller (1969) determine Igeo in the sediments. It is considered as qualitative pollution index analysis. Results indicate maximum average value for La and Ce with 14 and 12.8 representing extremely polluted sediments in the mining lake as shown in **Figure 4.6**.

Table 4.9: Enrichment factor (EF) and geo-accumulation index (Igeo) values calculated for sediments from ex-mining lake.

Parameters	Sc	Y	La	Ce	Pr	Nd	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Enrichment Factor (EF)															
UCC value	7	20	31	63	7.1	27	1	4	0.7	3.9	0.83	2.3	0.3	2	0.31
Average	5.7	0.4	48.5	0.4	12.7	0.0	30.7	0.1	13.4	0.4	23.2	0.2	119.0	0.3	100.8
Stdev	0.6	0.0	0.2	0.0	0.5	0.0	3.8	0.0	1.6	0.0	1.2	0.0	4.8	0.0	4.6
Min	4.7	0.4	48.1	0.4	12.2	0.0	24.0	0.1	11.8	0.4	21.7	0.2	110.2	0.3	91.0
Max	6.5	0.4	48.9	0.4	13.9	0.0	38.6	0.1	15.9	0.4	25.0	0.2	124.6	0.4	107.3
Range	1.7	0.1	0.7	0.0	1.7	0.0	14.5	0.0	4.1	0.0	3.2	0.0	14.4	0.1	16.3
Geoaccumulation Index (Igeo)															
Average	7.6	10.2	14.0	12.8	7.8	9.4	3.4	7.4	1.2	7.8	2.4	5.4	1.9	5.1	1.7
Std.dev.	0.2	0.1	0.0	0.0	0.1	0.1	0.2	0.1	0.2	0.1	0.1	0.0	0.1	0.1	0.1
Min	7.3	10.1	13.9	12.7	7.7	9.2	3.0	7.2	1.0	7.8	2.4	5.4	1.8	5.0	1.6
Max	7.8	10.2	14.0	12.9	7.9	9.5	3.7	7.5	1.4	7.9	2.6	5.5	1.9	5.2	1.8
Range	0.5	0.2	0.0	0.2	0.2	0.2	0.7	0.3	0.4	0.1	0.2	0.1	0.2	0.2	0.2
Median	7.6	10.1	14.0	12.8	7.8	9.4	3.4	7.4	1.1	7.8	2.4	5.4	1.9	5.1	1.7

Note: UCC value = upper continental crust value background value (Wedepol, 1995)

Table 4.10: Classification of Enrichment factor (EF), Geoaccumulation index (Igeo), Contamination factor (CF) and Pollution load index (PLI).

Classification of Enrichment factor (EF), Geoaccumulation index (Igeo), Contamination factor (CF) and Pollution load index (PLI)							
Enrichment Factor (EF)		**Geoaccumulation index (Igeo)**		**Contamination factor (CF)**		**Pollution load index (PLI)**	
EF	Class	Igeo	Class	CF	Class	PLI	Class
EF< 1	No enrichment	<0	Unpolluted	<1	Low contamination	0	Perfect
EF 1-3	Minor	0-1	Moderate polluted	1<CF<3	Moderate pollution	<1	Non polluted
EF 3-5	Moderate	1-2	Moderately	3<CF<6	Considerable pollution	>1	Polluted
EF 5-10	Moderately Severe	2-3	High pollution				
EF 10-25	Severe	3-4	Highly polluted				
EF 25-50	Very Severe	4-5	Extreme pollution				
EF >50	Extremely severe	>5	Extremely polluted				

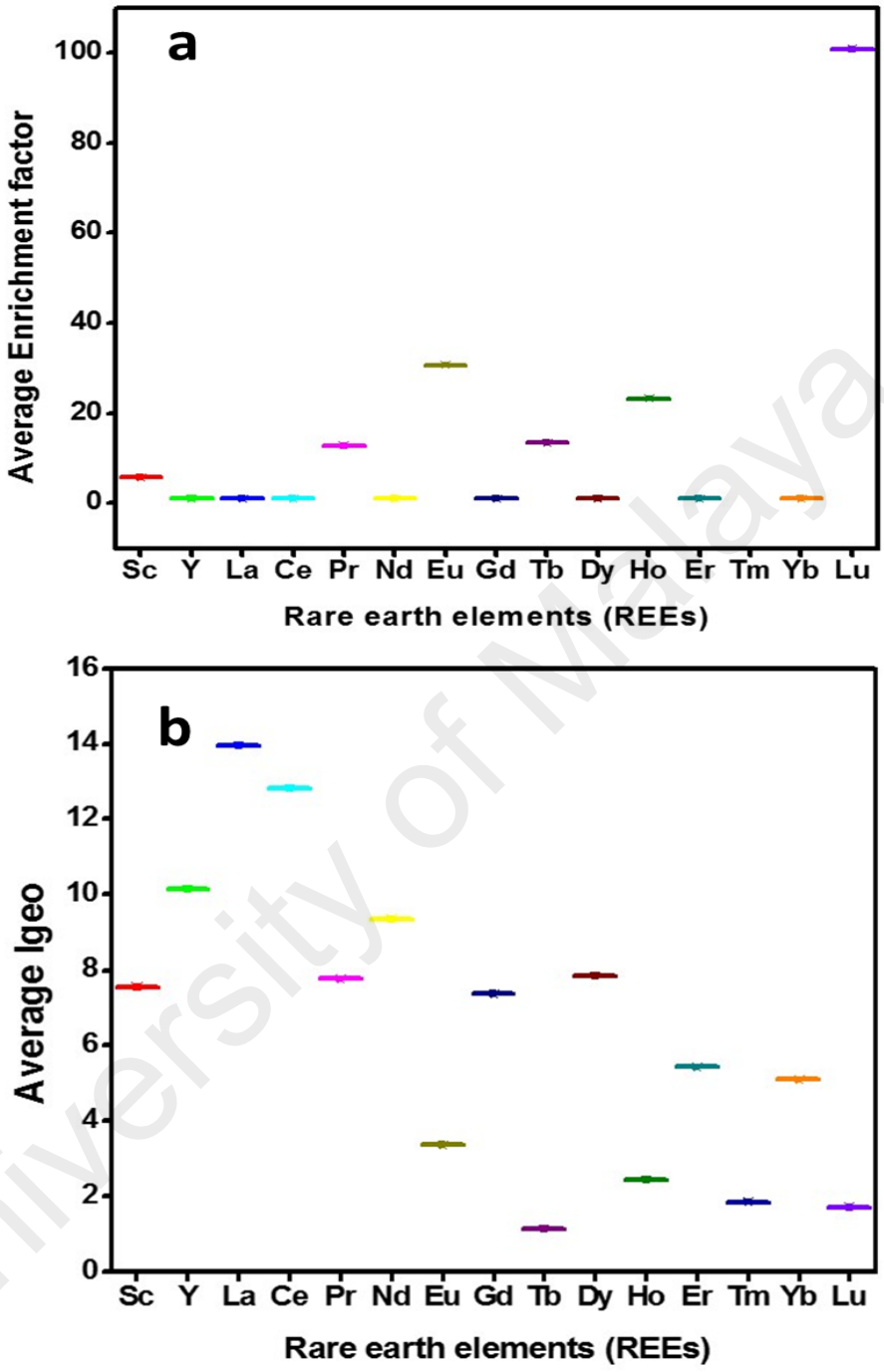


Figure 4.6: (a) Enrichment factor (EF) (b) geoaccumulation index (Igeo) in sediments.

4.2.3.2 Contamination Factor and Pollution Load Index (CF and PLI)

Contamination factor is also classified for its pollution level as shown in **Table 4.10.** The results from sediment analysis for contamination factor are represented in **Table 4.11** and **Figure 4.7** indicate that sediments in the mining lake are less deposited in Sc, Y, Pr, Ce and Nd and show considerable contamination. Sediments were much loaded with La, Eu, Gd, Tb, Ho, Er, Tm, Yb and Lu falling in the class very high contamination. Highest contamination factor was found in SD-6 for Tm (63.5) reflecting high contamination for all sediment samples.

Contamination factor (CF) and Pollution load index (PLI) gives very easy and simple evaluation of contamination level in sediments and is classified only into two classes. Sediments from mining lake were found rich in REEs as their pollution load index were very high. Highest PLI was noted at site SD-7 (17.41) indicating hazardous aggregation of REEs pollutants in the mining lake.

4.3 Soil Analysis

Rare earth elements (REEs) are widely distributed in the earth's crust and have an igneous, metamorphic, geogenic or sedimentary origin. These elements are transferred to the environment through natural but most often by anthropogenic sources (Babula et al., 2008). Accumulation of REEs in the soil is much more important due to their damaging and long-term hazardous effects (Liu et al., 2014). Soil pollution in urban areas due to mining of REEs is a major contributor to anthropogenic activity leading to damaging effects on nature and environment (Wang et al., 2001a).

In countries like Malaysia where equatorial or tropical climate with high temperature and heavy rainfall exist around the year, favor distribution and transport of REEs from source to the sink. Soil behaves as a sink for REEs by depositing particles released from industrial activities, mining, and automobile exhaust, etc (Hamzah et al., 2008).

Table 4.11: factor (CF) and Pollution load index (PLI) in sediment samples collected from ex-mining lake.

Sample	Sc	Y	La	Ce	Pr	Nd	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	PLI
UCC Value	7	20	31	63	7.1	27	1	4	0.7	3.9	0.83	2.3	0.3	1.96	0.31	
SD-1	6.46	4.26	24.68	2.79	6.28	1.36	16.33	15.94	6.54	22.30	11.27	12.11	56.17	14.62	50.81	16.79
D-2	5.45	4.44	24.89	2.85	6.37	1.43	14.25	15.27	6.73	23.66	11.20	11.83	58.70	14.37	52.55	16.93
SD-3	6.08	4.41	24.83	2.77	6.29	1.43	14.66	15.87	6.63	23.84	11.07	12.43	57.17	14.10	53.13	16.98
SD-4	6.57	4.33	24.85	2.83	6.78	1.35	16.78	15.75	7.87	22.91	12.71	12.65	63.50	13.35	46.35	17.24
SD-5	5.81	4.21	24.66	2.71	7.07	1.37	15.35	15.64	7.77	21.60	12.22	12.74	62.00	13.07	54.68	17.39
SD-6	6.30	4.53	24.68	2.68	6.57	1.25	12.25	16.04	8.10	22.99	12.65	12.50	61.20	12.53	49.84	16.94
SD-7	4.81	4.12	24.61	2.70	6.45	1.38	19.66	16.94	6.01	22.93	11.39	12.41	62.17	13.87	51.77	17.41
SD-8	5.50	4.17	24.63	2.71	6.23	1.37	16.65	15.94	6.49	21.86	11.95	11.96	62.00	12.50	53.39	17.16
SD-9	5.89	4.13	24.69	2.56	6.46	1.23	14.80	15.25	6.11	22.16	11.99	12.07	62.20	12.63	50.03	16.81
SD-10	4.91	4.01	24.52	2.75	6.30	1.32	15.75	13.74	6.03	22.09	11.75	12.04	61.40	12.61	51.10	16.69

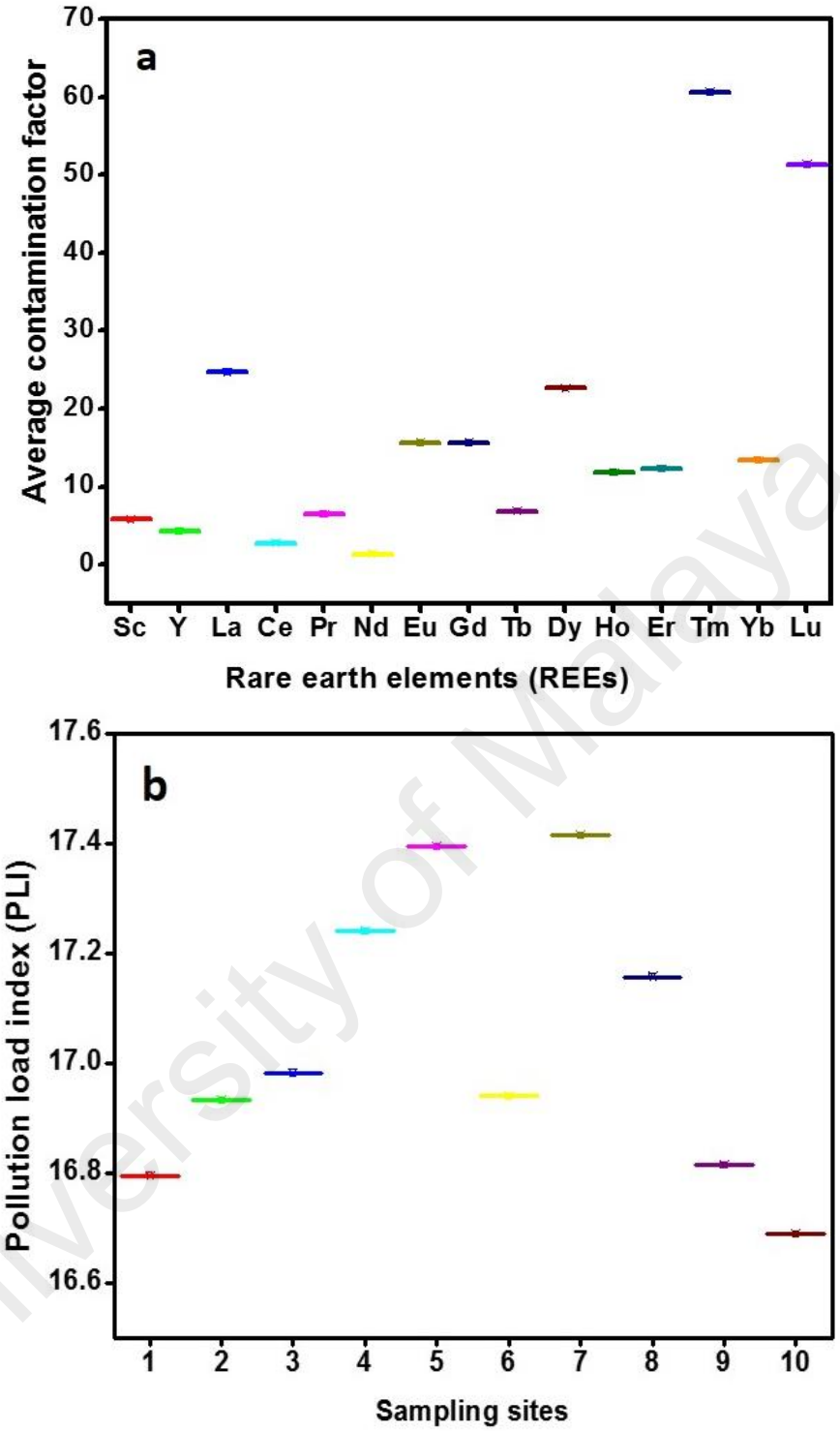


Figure 4.7: (a) Average contamination factor (CF) (b) Pollution load index (PLI) of REEs in sediments.

The exploitation of REEs in Perak may led to increasing levels of contaminants in the environment. This is one of the major causes of soil pollution (Liang et al., 2014).

In this study soil samples from forty different locations from ex-mining area in Perak were taken. Samples were collected from three different depths (0-20 cm, 21-40 cm, 41-60 cm) using auger. Soil sampling was done in 2014 to 2016 in three times fieldworks.

4.3.1 Physical properties of soil

REEs reach the surface of the soil, whether originated from any source. Physico-chemical properties, distribution patterns and speciation study, evaluate their providence in soil. Textural distribution and physical characteristics with three different depths of the samples have been studied. Physical properties are shown in **Table 4.12 & Appendix C.**

4.3.1.1 Grain size

Data analysis shows the high percentage of sand with average values 86 %, 85 % and 83.2 % in all samples with three depths (0-20 cm, 21-40 cm, 41-60 cm) respectively and some clay content is shown in **Figure 4.8**. Such condition allows excessive drainage and intensive leaching of soil ultimately lowering cation exchange capacity (CEC) and organic matter (OM).

4.3.1.2 Colour

Soil colour varies with depth. Soil collected from different locations was found with Mansell colour chart with 10YR4/3 brown, sandy clay, 7.5YR 8/0 silvery white, 10YR 8/8 yellow mustard, 5YR 5/8 orange red, 10YR 8/4 yellow beige, 10YR 3/3 brownish black, 5YR 7/8 orange brown, 5Y 5/1 dark grey and 10YR 2/1 dark black colour.

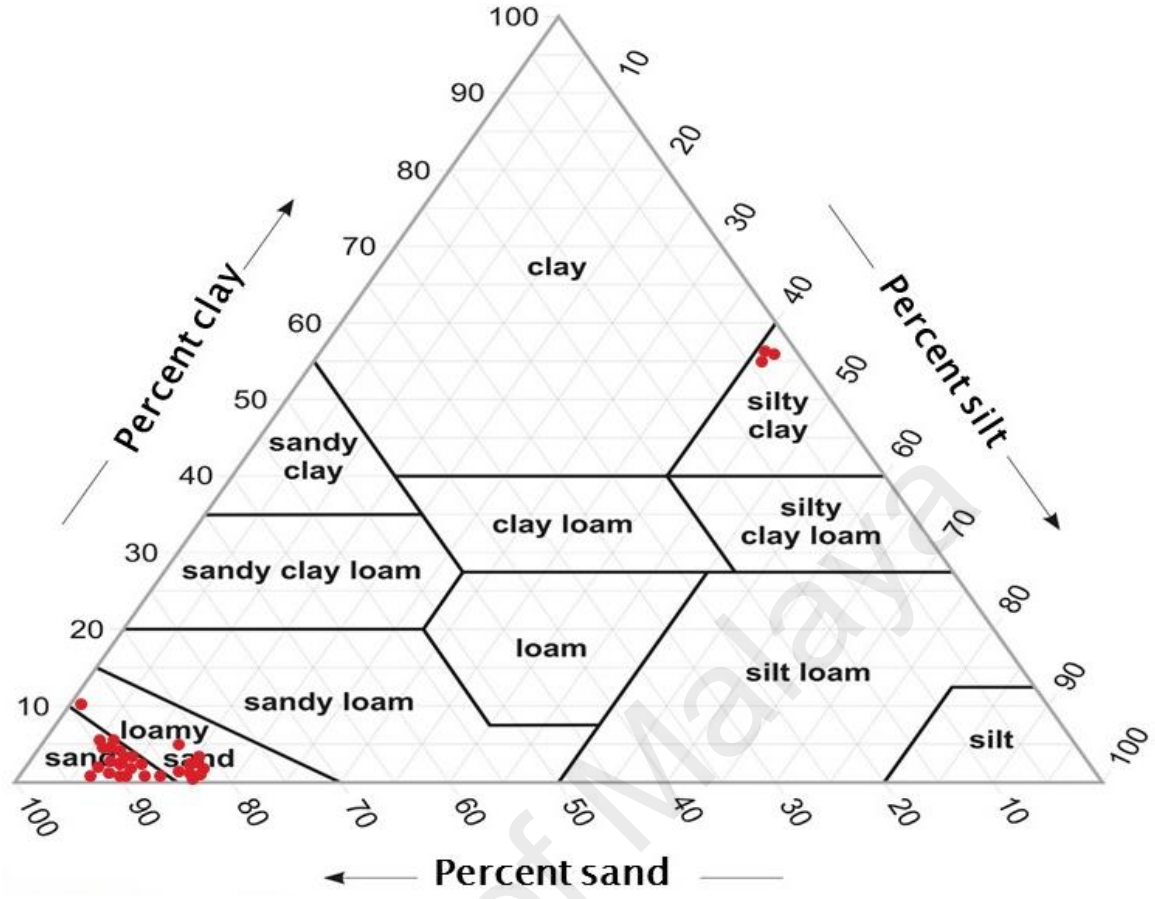


Figure 4.8: Distribution of soil samples grain size classification (n=40) in USDA soil classification diagram. Most of the soil samples were classified as sand type and some of the soil samples classified as silty clay type.

4.3.1.3 pH

pH is much lower in some soil samples with the lowest value of 3.0 at sampling site 12 but higher up to 8.3 at site 23**.** Lower pH value indicates negatively charged soil surface together with weathering of soil (Chutian et al., 2015). In contrast to tin mining areas in Selangor where pH is up to 3, the areas in Lahat have better soil pH as the problem of acidity does not arise. In fact, pH is too high in some sites. The high pH value may indicate the influence of limestone in some underlying deposits. Decrease in soil pH also decreases the REEs mobility and potential availability in the soil. CEC is generally low for soils having low clay content. Increase in organic matter content of the soil increases REEs potential availability and also enhance the CEC values (Medunić et al., 2014).

4.3.1.4 Electrical conductivity (EC)

Electrical conductivity (EC) found higher in most of the soil samples. Average EC values for all three soil depths vary as 55.85 µS cm^{-1}, 58.53 µS cm^{-1} and 56.56 µS cm^{-1} respectively. The maximum EC value was found to be 299.7 µS cm^{-1} in the second layer of soil (21-40 cm).

4.3.1.5 Cation exchange capacity (CEC)

A novel method for CEC shows good results for soil samples. The average value of CEC in the top layer (0-20 cm) of soil was found 17.06 cmol kg^{-1}, in the second layer (21-40 cm) was 17.28 cmol kg^{-1} while in the third layer (41-60 cm) was 17.36 cmol kg^{-1}.

4.3.1.6 Moisture content (MC)

Average moisture content (MC) of soil was also found in all three layers of soil and vary as 22.13 %, 24.13 %, and 25 % respectively.

4.3.1.7 Organic Matter (OM)

Organic matter content increases down the depth of soil. Maximum value was found at S14 (29 %) at the depth of 41-60 cm. However, all soil samples collected and analyzed for organic matter, it was found much lower compared to sandy. Mean values of physical parameters are shown in **Table 4.12**. Average values of organic matter for all three layers of soil ranged as 13.1 %, 15.05 %, and 15.60 %, respectively.

4.3.1.8 X-ray Fluorescence (XRF)

X-ray fluorescence (XRF) was studied for the elemental contents of soil given in **Figure 4.9** (**Appendix D).** The study area is flanked with alluvium cover after extensive weathering.

XRF analysis of clay indicates that sites with less than 50 % silica, about 30 % alumina. Calcium and magnesium oxides are generally low with 6 % and 3 % respectively. Oxides

of iron, titanium, tin, phosphorous, REEs also found in considerable percentages (Malaysia, 2011).

The study found similar patterns like ex-mining tin lands in Malaysia (USGS, 2011). This data give valuable information about the presence of metal compounds in the soil samples. Overall analysis reveals the disturbed soil profile due to mining activities, weathering processes, acid rain and heavy rainfall. These physical characteristics together keep soil, prevent from structure development. A currently structure of the soil in that area is massive and in time come to the structure developments until organic matter is present in considerable amount along with silt, sand, and clay.

4.3.1 Total Concentration of Rare Earth Elements (REEs)

Soil analysis reveals that in majority of the samples, the total concentration of REEs decrease with increasing atomic number and soil depth from the ex-mining area. Surface soil found rich in light rare earth elements (LREEs). The concentration (mg kg^{-1}) of REEs in surface soil (0-20 cm) determined was maximum for Ce, Nd, La, Y and Sc with 75.03, 62.90, 46.05, 38.12, 31.19 (mg kg^{-1}), respectively with decreasing trend for other REEs as shown in **Figure 4.10, 4.11** and **4.12.** Concentration of each rare element increase from 0-200 (mg kg^{-1}) shown by lighter to darkest grey color in the maps. Average, maximum and minimum concentration of REEs in surface soil (0-20 cm) have been given in **Table 4.13**. Subsoil (21-40 cm) was found enriched with Ce, Nd, La, Y and Sc but in less concentration than surface soil. Ce was found in highest concentration (41.61mg kg^{-1}). Deeper soil layer (41-60 cm) followed the same pattern of REEs as subsoil layer (21-40 cm). In this layer, Ce was found with 35.11 mg kg^{-1}. By comparing three soil layers, it can be concluded that distribution of Ce, Nd, La, Y and Sc is more significant than other REEs.

Table 4.12: Physical characteristics of the soil collected from three different depths from abandoned mines.

Depth	Parameters	No. of samples	pH	EC(µs/cm)	CEC(cmol/kg)	OM(%age)	Moisture Content (%)	Gravel (%)	Sand (%)	Silt and clay (%)
0-20cm	Mean	40	6.19	55.85	17.06	13.10	22.13	12.60	86.00	0.50
	Min		4.40	8.35	7.50	2.00	8.00			
	Max		7.80	276.20	32.00	28.00	39.00			
	Range		3.40	267.85	24.50	26.00	31.00			
	Median		6.55	25.37	14.75	12.00	20.00			
	Stdev		1.08	58.40	7.95	5.47	8.27			
21-40cm	Mean	40	6.09	58.53	17.28	15.05	24.13	12.20	85.00	0.60
	Min		4.20	7.24	7.00	4.00	8.00			
	Max		8.30	299.70	31.00	30.00	41.00			
	Range		4.10	292.46	24.00	26.00	33.00			
	Median		6.20	29.28	15.25	14.50	24.00			
	Stdev		1.19	61.81	7.79	5.81	8.15			
41-60cm	Mean	40	6.05	56.56	17.36	15.60	25.00	10.40	83.20	0.90
	Min		3.90	6.71	6.00	6.00	10.00			
	Max		8.30	273.50	33.00	29.00	42.00			
	Range		4.40	266.79	27.00	23.00	32.00			
	Median		6.05	25.93	15.75	15.00	25.00			
	Stdev		1.26	63.46	8.18	5.49	8.01			

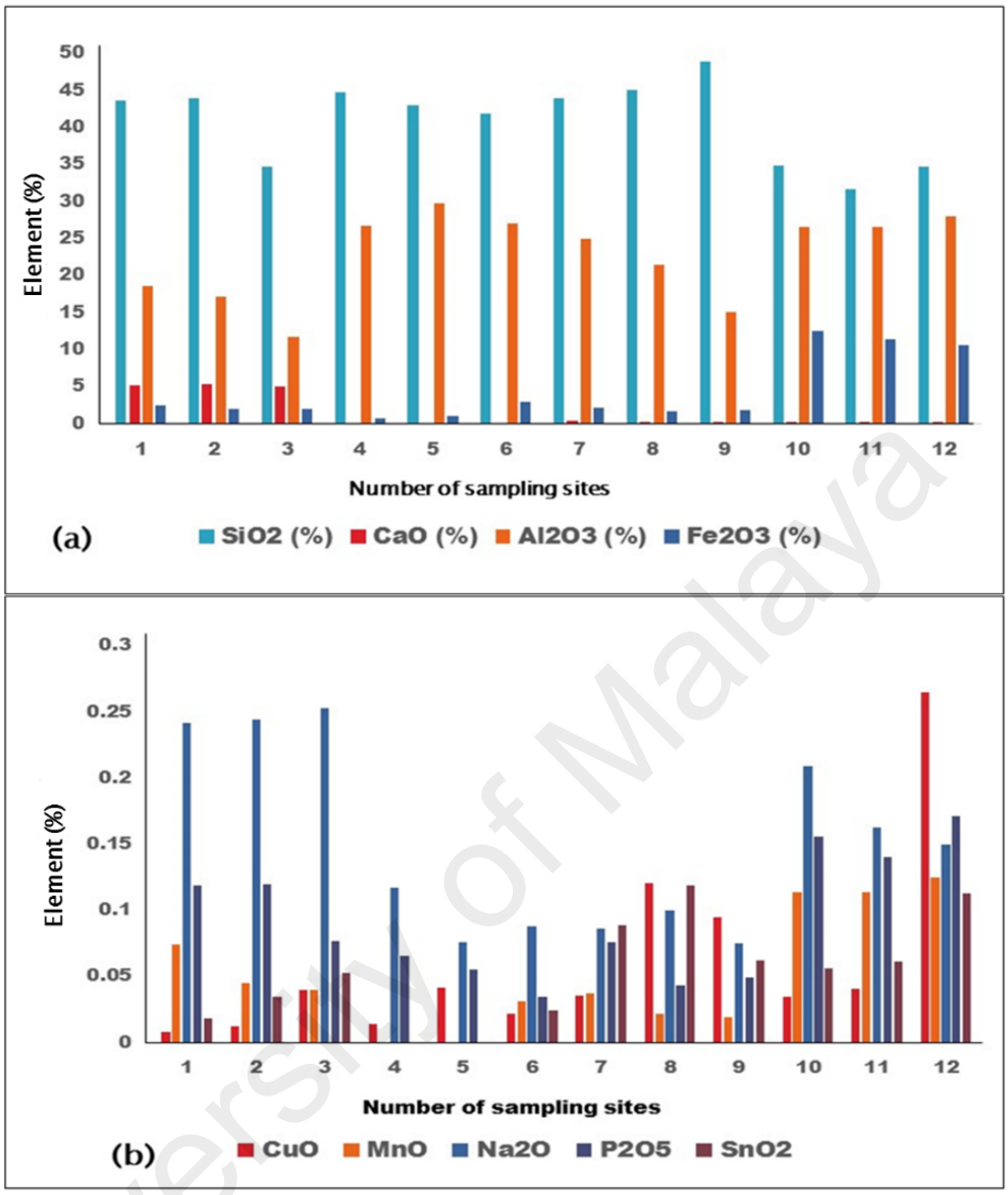


Figure 4.9: XRF analysis of soil with percentage of compounds.

The concentration of rare earth elements (ΣREEs) was higher in all the three depths of soil with the average value of 230.53, 196.55 and 377.66 mg kg^{-1} in the surface, subsurface, and deeper soils, respectively. These values are much higher compared to upper continental crust such as the average Post-Achaean Australian shale (PAAS, Taylor and McLennan 1985; ΣREE = 183 ppm) and global sub ducting sediment (GLOSS, Plank and Langmuir 1998; ΣREE = 137 ppm) (Taylor & McLennan, 1995, Hall et al., 1996) while in mining areas of China, Nd level up to 5726 mg kg^{-1} and 310 mg kg^{-1}. In soil,

natural crust level of Nd is 40 mg kg^{-1} (Jinxia et al., 2010). Abandoned mine soils in the SW of Spain investigated REEs and signify Ce, La, and Nd up to 82.1, 43.3 and 40.6 mg kg^{-1} which resides within the crystal structure of monazite (Fernández-Caliani et al., 2009).

Abandoned mine area in Perak represents high concentration for some REEs. A study reported by Khalid et al (2013) shows the contamination of soil with REEs (Ce, Sc, Y, and La) crossing the background values and mine waste was found responsible for soil contamination (Khalil et al., 2013). In surface soil REEs were present in same order of magnitude as suggested by (Taylor & McLennan, 1995).

4.3.2 Vertical distribution of REEs in different soil depths

REEs abundance in soils is influenced by factors such as soil structure, ancient material, weathering, OM, human activities, different reactions and pedogenic processes. In the Lahat, Perak soil samples, the average mean values and standard deviations of detected concentrations of REEs are presented in **Table 4.13** and **Figure 4.13.** The concentration and distribution of REEs in the soil depend on its different types and mining activities. The REEs concentration largely influenced by atomic number. REEs with even atomic number are in excess than odd atomic number (Wang & Liang, 2015).

The data describe the high concentration of cerium, neodymium, yttrium and scandium in all surface soil samples (0-20 cm). This may be due to the previous mining activity byproducts, monazite and xenotime minerals present in the soil of the area. Major resources of REEs are bastnasite, monazite, loparite and lateritic adsorption clays. In the soils of Baotou mining area in China, the concentration of REEs ranged from 156 to 5.65 x 10^4 mg kg^{-1} (Wang & Liang, 2015). However, with increasing depth, in subsurface soil layer (21-40 cm) most of the REEs decrease in concentration and become constant for some elements.

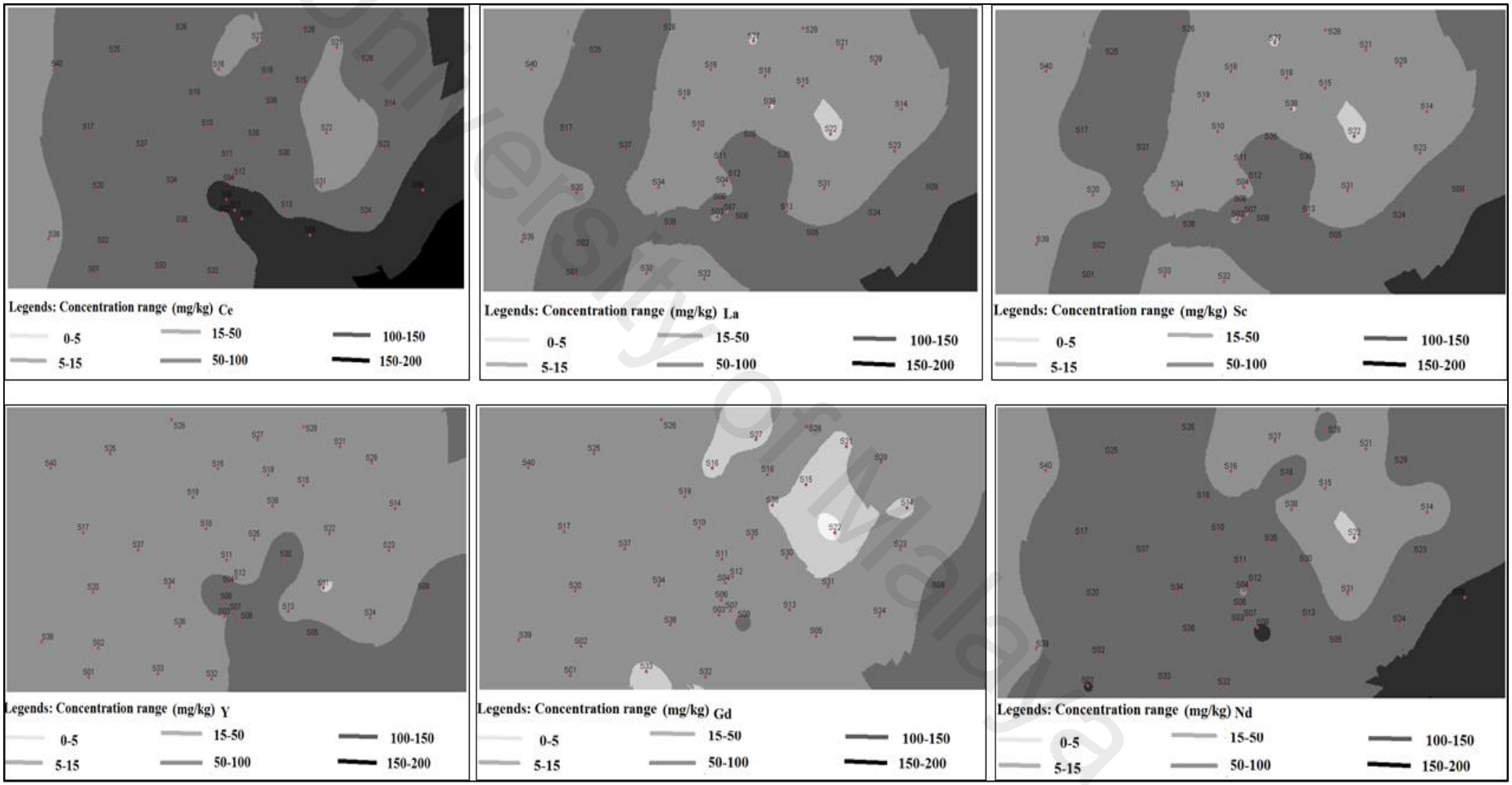


Figure 4.10: Rare earth elements (REEs) distribution in the surface soil specifically Ce, La, Sc, Y, Gd and Nd**.**

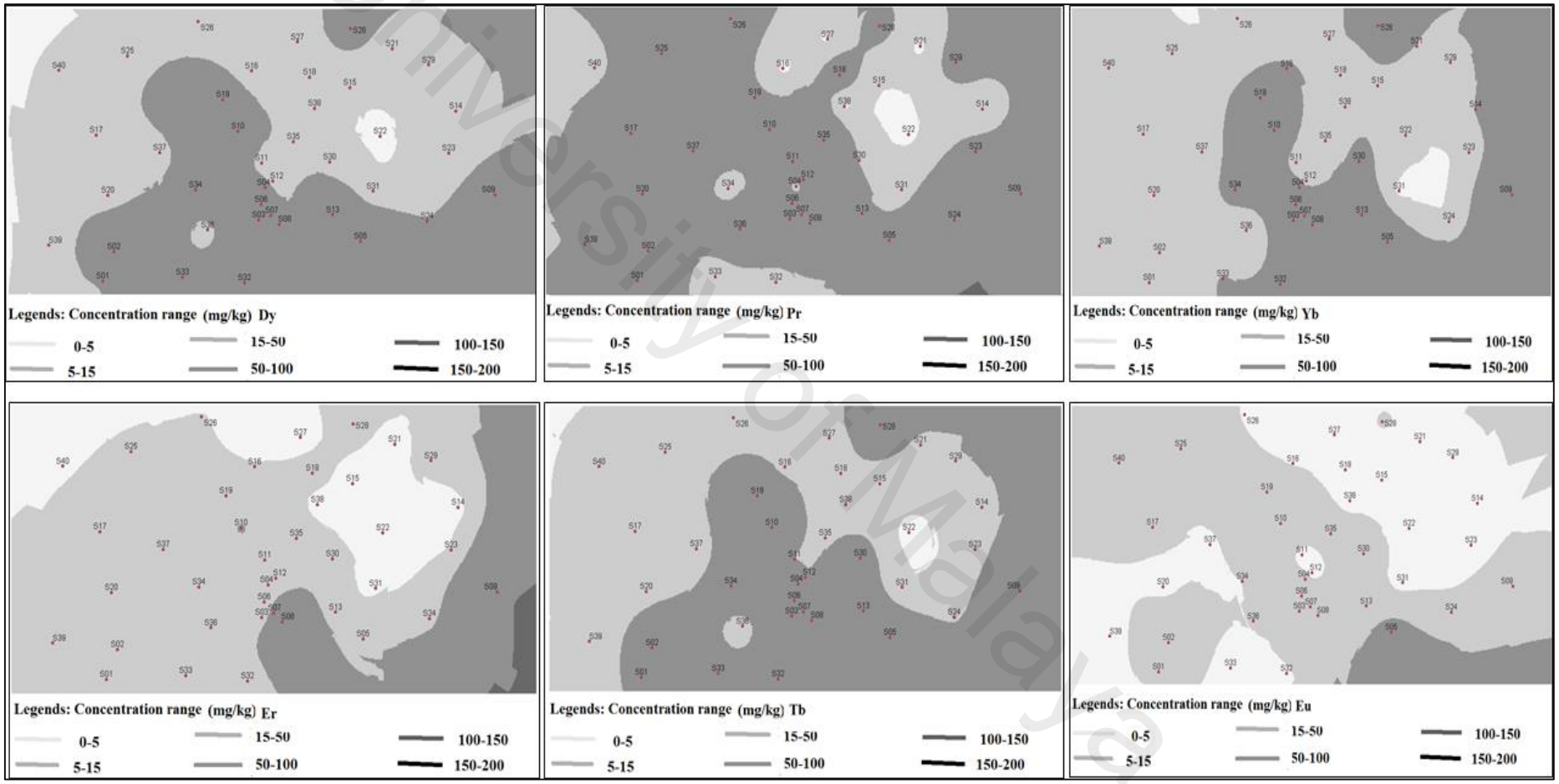


Figure 4.11: Rare earth elements (REEs) distribution in the surface soil specifically Dy, Pr, Yb, Er, Tb, and

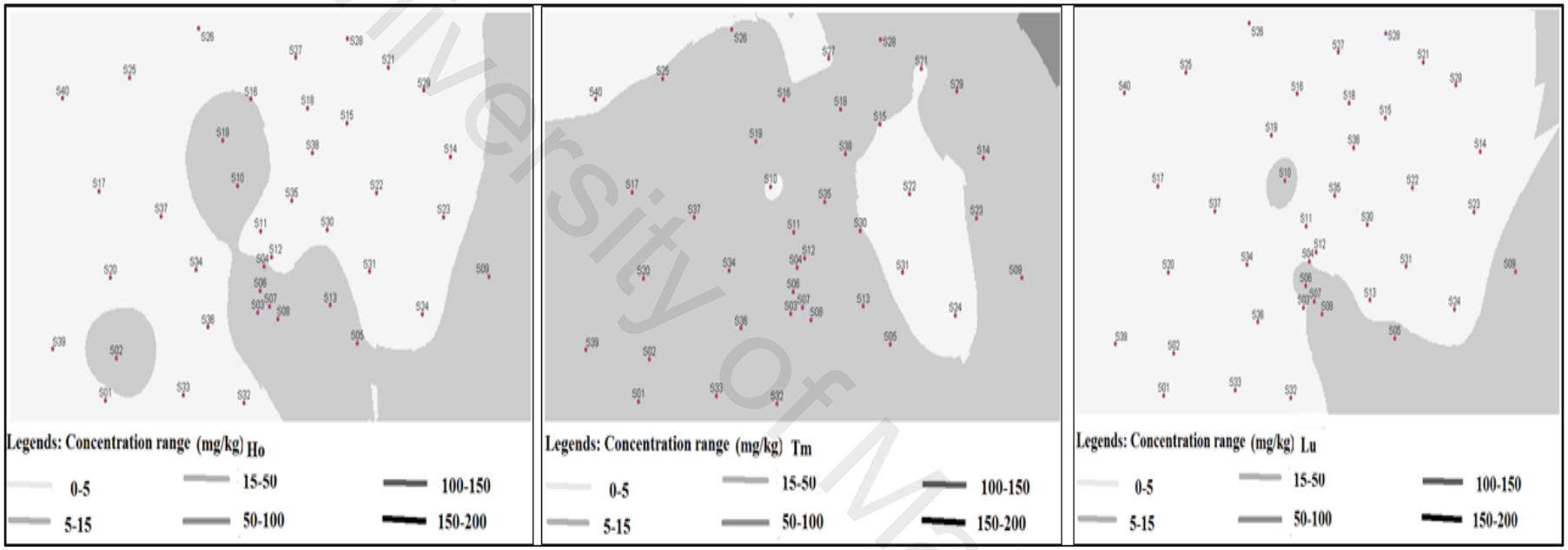


Figure 4.12: Distribution of holmium (HO), thulium (TM), and lutetium (Lu) in the surface soil.

Lower layer (41-60 cm) studied show somewhat similar values with sub surface of soil. Average concentrations measured in Sweden soil also show 25.3 mg kg^{-1} of LREEs abundance with La, Ce and Nd, and 53.6 mg kg^{-1} in subsoil surface (Sadeghi et al., 2013).

Generally, cerium (Ce) and neodymium (Nd) being highest in concentration while holmium (Ho) and lutetium (Lu) in lowest concentration were observed. Results show similarity with Muhammad et al. (2015).

Soil samples found rich in light rare earth elements (LREEs) like Ce, Nd, Pr, La) as compared to high rare earth elements (HREEs) from gadolinium to lutetium (Humphries, 2013). Some anomaly also found in inverse relation down the earth. Certain elements have a slightly more concentration in three depths. Sc, Y, La, Nd, and Ce have slightly higher concentrations in 0-20 cm depths from the surface while their concentration decreases with depth (Fiket et al., 2016). Results strongly follow Oddo- Harkins rule. This can be concluded from **Figure 4.13.**

Distribution of REEs is much more common from S01-S10 and S13, S28, S33, S34 due to the place around the mining lake and mining area (Goonan, 2011). Sampling locations with the natural origin (S24-S28 and S36) have been found high amount of REEs after mining land. The reason is that mining area converted into palm oil plantation after reclamation. Lots of fertilizers added to make the land fertile. After an industrial application of REEs now, REEs are also utilized in fertilizers. Increasing utilization in agriculture leads to the increased REEs into the ecosystem and food chain (Torrisi, 2014) through soil accumulation, crops bioaccumulation. Populated areas generally found in low rare earth concentration distribution levels. This may be due to the construction and removal of original soil profiles in that area (Nicoletopoulos, 2014).

Table 4.13: Average concentration (mg kg^{-1}), standard deviation, minimum and maximum values of REEs in different soil depths.

Parameters	**Depth**	**Sc**	**Y**	**La**	**Ce**	**Pr**	**Nd**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	Lu
Average values	0-20 cm	31.19	38.12	46.05	75.03	19.19	62.90	6.45	24.81	18.02	15.45	4.18	9.30	8.30	15.81	2.86
Minimum		10.22	11.75	11.41	27.68	3.15	12.62	1.36	2.55	2.05	4.17	1.02	1.35	1.18	3.19	0.65
Maximum		51.47	84.70	95.16	159.50	37.16	112.30	21.72	61.02	42.26	37.37	12.45	47.35	14.28	41.32	9.33
Std.dev.		6.14	5.72	2.56	4.61	0.27	2.25	0.29	1.03	0.89	0.11	0.53	0.97	0.66	1.35	0.37
Average values	21-40 cm	19.32	30.84	27.13	42.68	9.41	35.45	4.56	13.71	12.86	10.30	2.81	4.44	5.26	11.40	2.17
Minimum		7.65	7.66	8.18	7.43	2.05	11.30	1.55	4.66	3.21	3.99	0.85	1.20	2.76	1.79	0.84
Maximum		30.32	70.36	76.34	92.07	23.04	60.18	16.02	23.65	25.51	28.74	7.96	10.35	8.84	28.66	5.96
Std.dev.		1.43	1.52	2.34	1.98	0.72	2.18	0.15	1.17	2.62	0.71	0.27	0.12	0.22	0.02	0.39
Average values	41-60 cm	17.19	26.17	24.51	35.11	7.49	31.57	3.53	10.67	10.77	8.16	2.52	4.39	3.98	9.65	2.07
Minimum		6.48	6.98	6.33	6.05	1.86	9.78	1.01	2.00	3.07	2.57	0.69	0.08	1.06	1.36	0.09
Maximum		28.90	69.48	69.43	89.75	20.69	55.28	14.07	19.05	24.74	17.82	7.75	13.68	6.87	25.32	5.70
Std.dev.		1.30	1.12	1.21	1.01	0.14	0.24	0.36	0.33	0.89	0.06	0.14	0.01	0.33	0.34	0.02

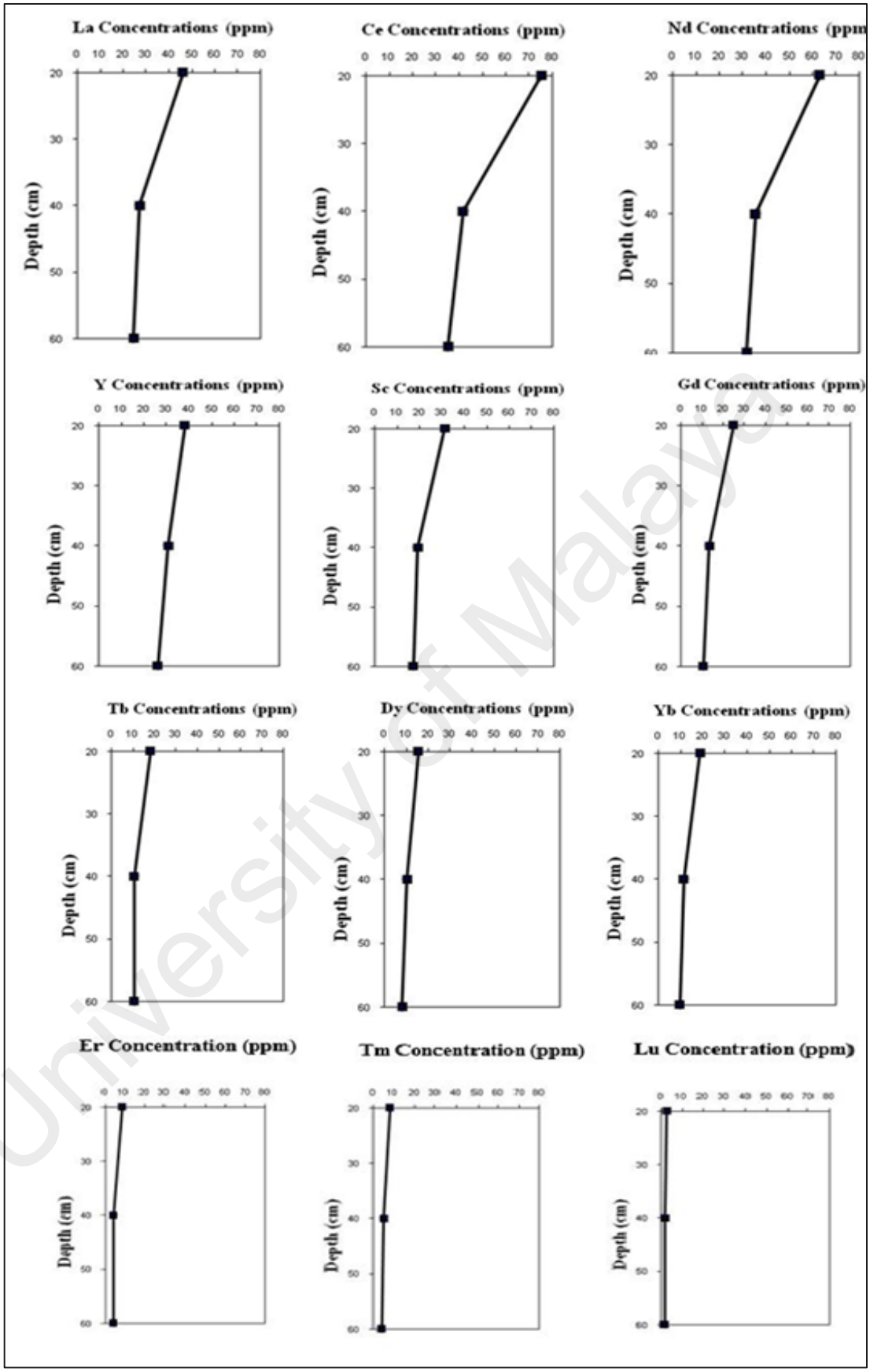


Figure 4.13: Average concentration variation of some REEs in different depths.

Recreational places near residential have been seen with considerable amounts of REEs which is a very bad signal to the young population residing in that area. Results indicate REEs concentration high in the ex-tin mining area but variations have been observed with the distance from the source (Charalampides & Vatalis, 2015).

Different studies showing mean values for soil REEs were found similar to previous studies. REEs in the soil surface and earth crust were found quite similar in magnitude (Taylor & McLennan, 1995). In most cases lowest values are observed in sandy soil compared to loamy. Potential mobility of REEs enhanced by their high presence in silicate and residual fraction. Sandy soil containing high silica content show positive behavior for REEs mobility whereas loamy soil due to its fertility, complex and compact structure with different REEs decrease their mobility but increase bioavailability.

Generally, acidic soils contain less REEs than alkaline soil. However, REEs in different soils indicate the strong positive correlation with each other. From the (Figure 4.7), it is clearly seen that the trace metals are more deposited in the upper soil surface. Other two depths 21-40 cm and 41-60 cm have about equal concentrations of REEs. There is an abrupt change in rare earth along the depth but at some sites increase in concentration also observed for increasing soil depth. Decreasing concentration with increasing depth range in the order Ce > Nd > La > Y > Sc > Gd > Tb> Dy >Yb. While average concentrations of REEs in surface soils in mining area of China show Ce > La > Nd > Pr > Sm > Gd > Dy > Er > Yb > Eu > Tb > Ho > Tm > Lu (Cheng et al., 2011, Cheng et al., 2013). It can also be concluded that light rare earth (LREEs) are more common in soil samples of current study area than heavy rare earth (HREEs).

In the deep soil (21-40 cm) Tb and Tm have higher EF average values with 48.35 and 43.29 meaning that Tb increasing with depth, showing very severe enrichment. Yb and Lu show severe enrichment while the rest of REEs has moderately severe to minor

enrichment in this soil depth profile. Deeper into the soils (41-60 cm), enrichment factor increases for all REEs compared to subsoil surface. Tb and Tm show average enrichment factor of 83.18 and 71.77 respectively. Average values of Yb and Lu varies as 26.61 and 36.05 while average EF values for Eu, Gd, Dy, Ho, and Er are 19.1, 14.42, 11.31, 16.44 and 10.32 respectively. Y, Sc, La, Ce, Pr, and Nd show minor to moderately enrichment factor with average values 7.07, 2.79, 4.27, 3.01, 5.71 and 6.32 respectively. Such distribution may be related to many sources of pollution mainly focusing on mining in that area, agriculture, and expansion of tin mining anthropogenic activities in the area (Liang et al., 2014). These results describe extant evidence of ex-tin mining sites in Kinta district, especially in the Lahat, Kampar, Batu Gajah, Taman Bukit Merah, Menglembu and Kota Bharu areas. Average I*geo* values show elevated amounts of REEs in the soil, suggesting area heavily polluted.

Geoaccumulation index appear to be in last category having values greater than 5 indicating severely polluted with rare earth where *Cn* is the concentration of the element in the sample and *Bn* is the background value of the element based on (Gao et al., 1998). Almost all REEs are mostly accumulated in the upper soil surface and decrease with depth. This area already nominated as contaminated by Akif et al. 2014.

4.3.3 Statistical Analysis

Statistical data analyses were carried out using the data analysis software, JMP version <pro 12.0.01>SAS institute Inc., Cary, NC, U.S.A, 2015 software. PCA was applied to the data in order to map the soil samples' REEs and the physical parameter distribution based on the different soil depths.

4.3.3.1 Box plot of soil samples from different depths of ex-tin mining ponds in Perak

Based on the results of the PCA, a test was carried out to ascertain the differences between the physical and chemical parameters from the different sampling depths. To test for the differences in the physical and chemical characteristics between the different depths, one-way analyses for comparing means was conducted, and the significance of the results was tested for all pairs Tukey HSD at 95% confidence interval.

The p-values for each soil depth are noted for all the parameters studied in the **Table 4.14**. For p-values which are less than 0.05 denote a significant difference between the mean values of two soil depth groups, while p-values which are larger than 0.05 shows that the means of the two soil depths being compared are significantly similar. The variations in the values of the physical and chemical parameters are plotted in a boxplot, as shown in **Figure 4.14** (a, b, c, and d).

The physical parameters such as pH, EC, and CEC are significantly ($p>0.05$) similar in all three depths and this can be observed from the box and whisker plots as well. It is understood that for sandy soils with less clay and organic matter content, the physical parameters remain low with base cations associated with the soil carbonate content. However, comparison of OM values between the depths of 0-20 cm and 41-60 cm (0-20 cm vs 41-60 cm) and (0-20 cm vs 21-40 cm) show that they are significantly ($p<0.05$) different from one another. While, those between depths of 21-40 cm and 41-60 cm are significantly ($p>0.05$) similar due to similar soil particle arrangement and their undisturbed nature. This is observed in **Figure 4.14 (a)** as inter-quartile range (IQR) for samples from the depth of 0-20 cm is lower than the other two depths and has smaller median values.

Table 4.14: Significance of physical and chemical parameters in soil samples.

Parameters	p- values between different soil depths		
	(0-20 cm vs 41-60 cm)	(0-20 cm vs 21-40 cm)	(21-40 cm vs 41-60 cm)
pH	0.5485	0.7599	0.9385
EC (µs/cm)	0.9404	0.9670	0.9958
CEC(cmol/kg)	0.9675	0.9798	0.9985
Organic Matter (%age)	0.0018	0.0213	0.7196
Moisture Content (%age)	0.0275	0.1640	0.7273
Sc	<0.0001	<0.0001	0.1298
Y	<0.0001	0.0057	0.1158
La	<0.0001	<0.0001	0.4342
Ce	<0.0001	<0.0001	0.0829
Pr	<0.0001	<0.0001	0.0713
Nd	<0.0001	<0.0001	0.2794
Eu	<0.0001	<0.0001	0.0905
Gd	<0.0001	<0.0001	0.0346
Tb	<0.0001	<0.0001	0.0331
Dy	<0.0001	<0.0001	0.0209
Ho	<0.0001	0.0002	0.1815
Er	<0.0001	<0.0001	0.9675
Tm	<0.0001	0.0004	0.5451
Yb	<0.0001	0.0005	0.2779
Lu	<0.0001	0.0032	0.5018

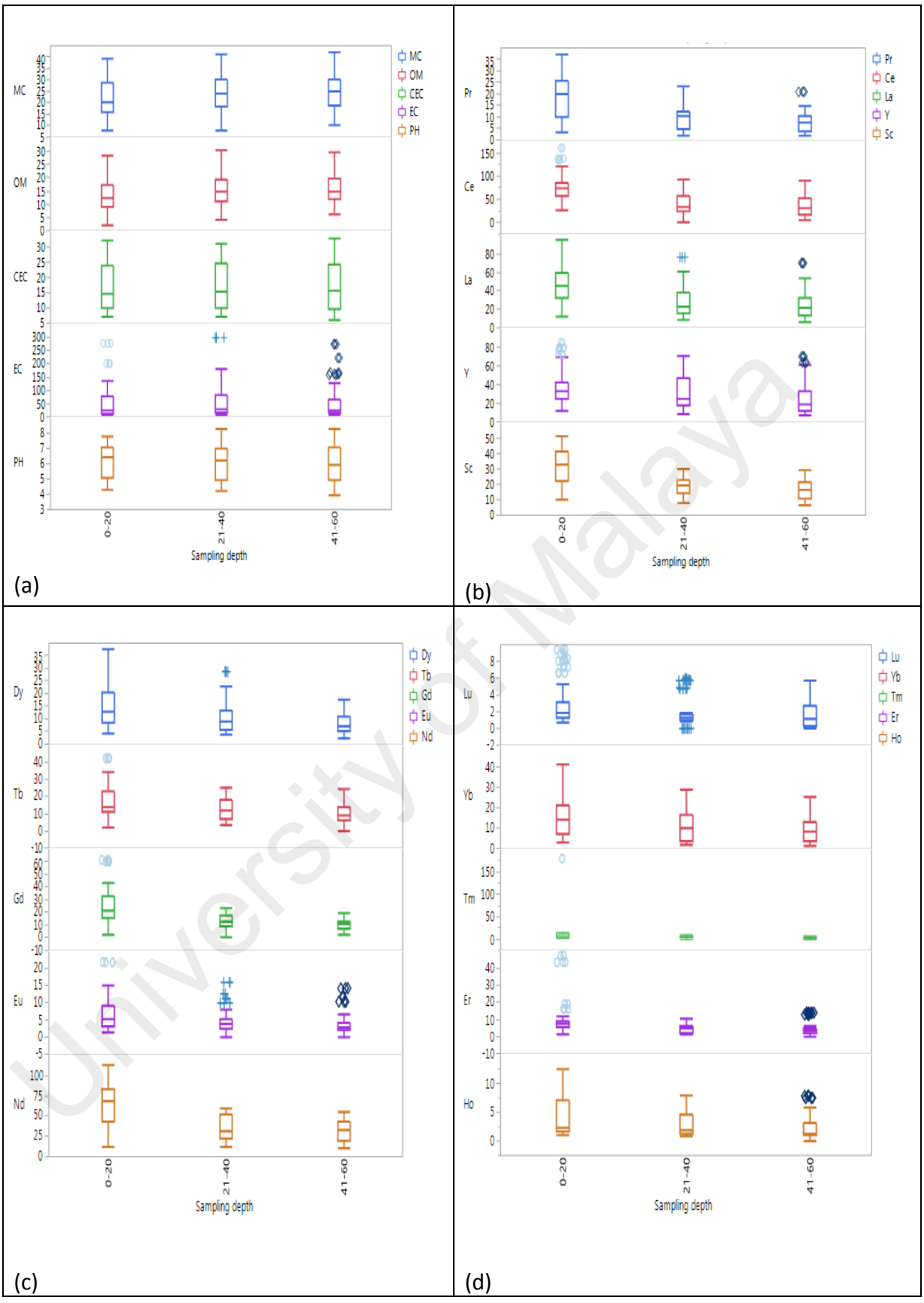


Figure 4.14: Boxplots of REEs in surface soil (a) physical parameters; (b, c, d) chemical parameters**.**

Moisture content (MC) is another physical parameter that has significantly similar values with the (0-20 cm vs 41-60 cm) depths, while the other two groups [(0-20 cm vs 21-40 cm) and (21-40 cm vs 41-60 cm)] has significantly similar values. This could be explained by the low water content of soil with lesser compactness, and high sand percentage that could easily allow water percolation through soil. This can be clearly seen from the boxplot of **Figure 4.14 (a),** where the IQR range is approximately similar. The median at the depths of 21-40 cm and 41-60 cm are in the same range, but for the depth of 0-20 cm, the median is lower and closer to the lower values due to mining activities that had taken place over a long period of time.

In the case of chemical parameters, comparing samples at the depths of (0-20 cm vs 41-60 cm) and (0-20 cm vs 21-40 cm), they are significantly ($p<0.05$) different while those at the depths of (21-40 cm vs 41-60 cm) are significantly similar ($p>0.05$) except for Gd, Tb and Dy that are the same which is observed from boxplots in **Figure 4.14 (b, c and d).** This could be explained by taking into consideration that these REEs are a part of the monazite mineral used in many industries for mechanical manufacturing.

4.3.3.2 PCA based on the depth of sampling points

PCA was applied to a matrix of 20 variables and 360 samples. These soil sample data from the state of Perak have been seen to cluster based on the sampling depth. 4 principal components with eigenvalues>1 were extracted explaining a total variance of 60.4 %. **Figure 4.15** shows the biplot of soil samples collected from three different depths of 0-20 cm, 21-40 cm and 41-60 cm. From the PCA, two main clusters are observed. Cluster 1 consists of samples from the depth of 0-20 cm, while samples from the depth of 21-40 cm and 41-60 cm are identified as cluster 2.

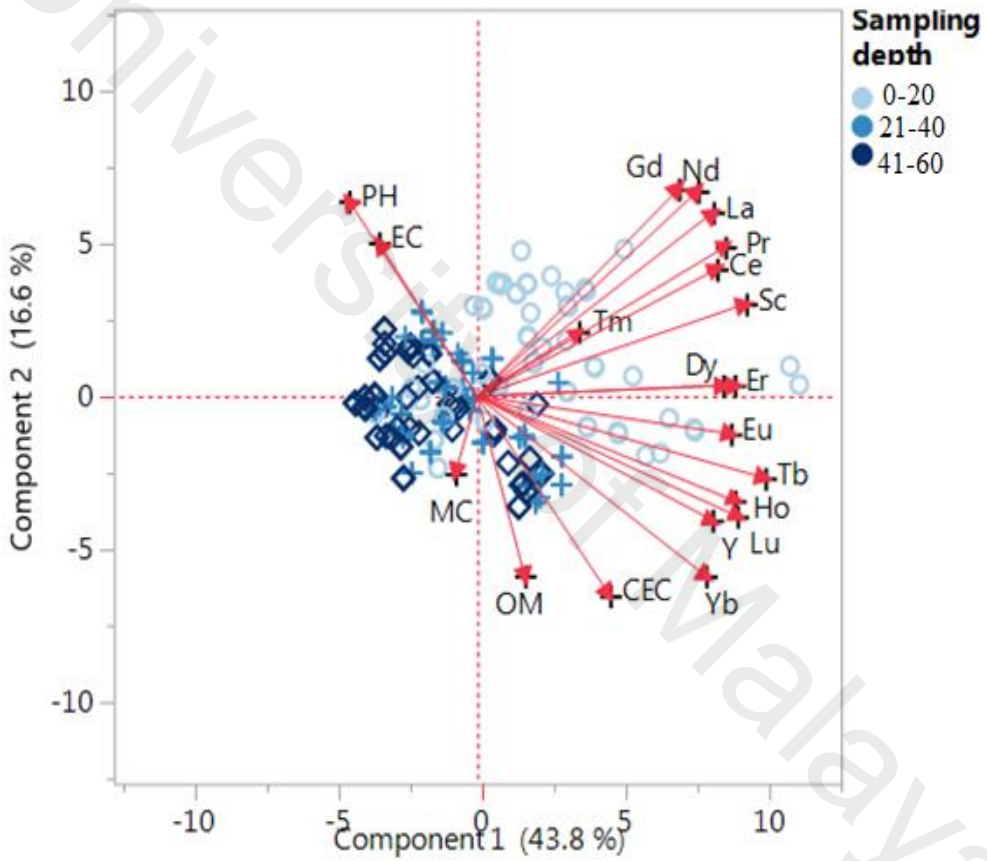


Figure 4.15: The biplot of soil samples collected from three different depths of 0-20 cm, 21-40 cm and 41-60 cm.

Moreover, visual inspection of colour of the soil samples can gives us the same clustering. Soil samples at depths of 0-20 cm had a lighter colour compared to two other depths which had fairly the same colour and were clustered in one group. This could be explained by the presence of iron sulphates mixed with middle and deeper soils which were absent in surface soil. As well, it might be due to limestone and alluvium bedrocks covers.

Separation of samples in clusters 1 and 2 are mostly based on the scores of the first principal component (PC1). From the plot, it can be observed that although the samples from the depth of 0-20 cm are spread out, there are still samples at the right hand side of the graph. Samples in this cluster are mostly loaded by Gd, Nd, La, Pr, Ce, Sc, Tm, Dy, Er, Eu, Tb, Ho and Lu. Samples taken from the depth of 21-40 cm and 41-60 cm are mostly located at the left hand side of the plot, and are loaded by MC, EC, and pH, while a small number of samples in this cluster are loaded by OM and CEC. It can be concluded that the rare elements are the main discriminating factors for the separation of soil samples at the depth of 0-20 cm from the others. It can also be observed that at depths of 21-40 cm and 41-60 cm, the soil profile in terms of rare earth elements is rather similar. This conclusion is made based on the fact that the samples from these depths are inseparable in the scores plot. The discriminating factors of samples in cluster 2 are the physical parameters of pH, EC, OM, and CEC. The PCA was further applied to the samples of cluster 2 to see if these two groups are separable from one another, but it was observed that soil samples at depths 21-40 cm and 41-60 cm cannot be separated.

The results in the current study conclude that REEs concentration in surface soil is high compared to other soil depths. Concentration range for surface soil vary between 2.86 to 75.03 mg kg^{-1}. This layer (0-20 cm) has greater concentrations of REEs compared to other two layers (21-40 cm, 41-60 cm). Some REEs such as Ce, La, Nd, Gd, Sc, and

Y were consistently higher throughout the soil. In general, soil physical properties contribute more to the high concentration of rare elements in the surface soil. PCA revealed clustering of soil samples into two clusters and the discriminating factors between the clusters are Er, Dy, Sc, Eu, Tb, Ho, Lu, Tm, Ce, Pr, La, Nd and Gd. Indeed, mapping the soil samples according to sampling depths was possible by PCA. Investigating the physical and chemical properties of the different depths between each other was done by one way analysis using all pairs Tukey HSD with 95% confidence interval. It is noted that physical parameters such as pH, EC and CEC are significantly similar ($p>0.05$) in all three depths suggesting that the information on these three parameters can be obtained from analyzing any layers of soil whereas Gd, Tb and Dy are the only chemical parameters that are significantly different ($p<0.05$) in all the three depths. This shows that in order to obtain information on these parameters, analysis of three different depths is required. For Sc, Y, La, Ce, Pr, Nd, Eu, Ho, Er, Tm, Yb, Lu and OM (21-40 cm vs 41-60 cm) depth comparison, there is no clear trend in terms of similarity and dissimilarity. MC is the only physical parameter that show significantly similar values for (0-20 cm vs 21-40 cm) and (21-40 cm vs 41-60 cm.) The comparison for (0-20 cm vs 41-60 cm) is significantly different.

4.3.3.3 Hierarchical cluster Analysis (HCA)

Hierarchical cluster analysis is an important means to investigate the distinctiveness of REEs concentrations in the soil environment, especially for environmental qualities (Xue et al., 2013). HCA was also applied to all the samples in this work. It is observed from **Figure 4.16** that there are two main clusters which follow the grouping of PCA. Ward's method was used for obtaining the histogram applied to 360 samples.

Samples in cluster 1 are mainly from the 0-20 cm depth. In this cluster nearly all the rare earth elements are present and in close relation with each other shown by a light blue

color while those in cluster 2 are from the depths of 21-40 cm and 41-60 cm shown by darker blue circles. HCA also indicates that some of the elements from the subsoil and deeper soil layer are in relation with the elements from the surface soil. This follows the clustering obtained from PCA, which indicates that the conclusions obtained from the principal component analysis are sufficient in understanding the profile of the samples in this work. REEs bearing minerals such as monazite, xenotime etc. are present across the Lahat, Menglembu, Kinta Valley, Perak renowned as former tin mining and ex-mining areas in Malaysia.

Concentration of Ce was found high in all the soil layers studied with highest in the surface layer (0-20 cm) and positively correlated with monazite mineral. Other REEs have also been found which indicate that soil loaded with REEs which acts as a sink of pollution. Moreover, separation of soil samples based on sampling depths into two clusters was made possible by PCA and HCA. Separation is observed between samples collected near the surface (0-20 cm) compared to samples collected from the deeper soil. The discriminating factors are the concentrations of the rare elements La, Ce, Gd, Nd, Tm, Pr, Sc, Er, Eu, Tb, Ho, Lu, Yb, and Dy. Different environmental risk assessment has shown that top soil is much polluted with rare earth, but less polluted in deeper layers. It conclude from the study that REEs in high concentration deposited in different depths of soil profile could be a source of these elements and their environmental risk impacts could be reduced by different techniques to save humans and other living organisms present in terrestrial as well as aquatic ecosystem.

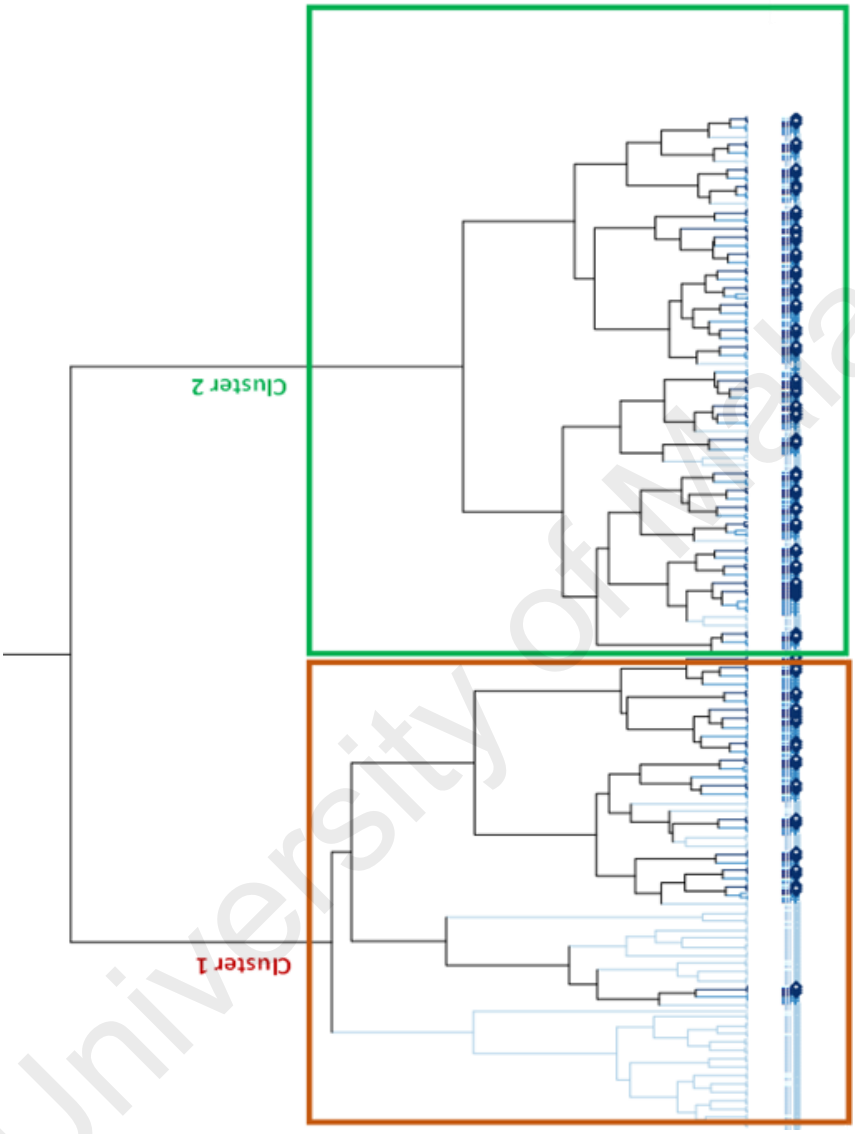


Figure 4.16: Hierarchical cluster Analysis (HCA) following PCA with two major clusters.

4.3.3.4 Variables of REEs based on land use

PCA was applied to a matrix of 360 samples and 20 variables. Five principal components with eigenvalues >1 were extracted explaining (61.1) % of total variance. Soil samples from ex-mining areas of Perak Malaysia have been mapped according to the concentration of rare earth elements and physical properties of pH, EC, CEC, OM and MC.

Figure 4.17 (a) illustrates the biplot of soil samples from different sampling areas of 'industrial', 'mining', 'residential' and 'natural' at the surface soil (0-20 cm). From the PCA, four main clusters are observed. Although some of the samples from each group are spread out but in general, the samples from each group are seen to be more populated on one side. Samples from 'industrial' area have both negative PC1 and positive and negative PC2. pH, EC and MC are the most dominant parameters for discrimination of samples in 'industrial' area of surface soil from mining, natural and examining areas in 0-20 cm depth. The mean concentration of rare elements and the values of physical parameters for surface soil (0-20 cm) is listed in **Table 4.15**.

Most of the samples from the 'natural' area have positive and negative PC1 as well as positive PC2. In other words, PC1 is responsible for the separation of samples in the 'natural' area from other two groups of 'mining' and 'residential'. The most important factor in this separation is the electrical conductivity (EC) and the concentration of Pr. Samples from the 'residential' area are mostly located at the lower left hand side of the quadrant having negative PC1 and PC2. In other words, both PC1 and PC2 are responsible for the separation of most of the samples in this area from the other three groups. This separation is mainly due to the lower concentrations of Pr, Sc, Tm, Nd, Gd and La. While most of the samples in residential area are enriched in MC. Furthermore, samples from the 'mining' area spread out and mostly located at lower half of the graph.

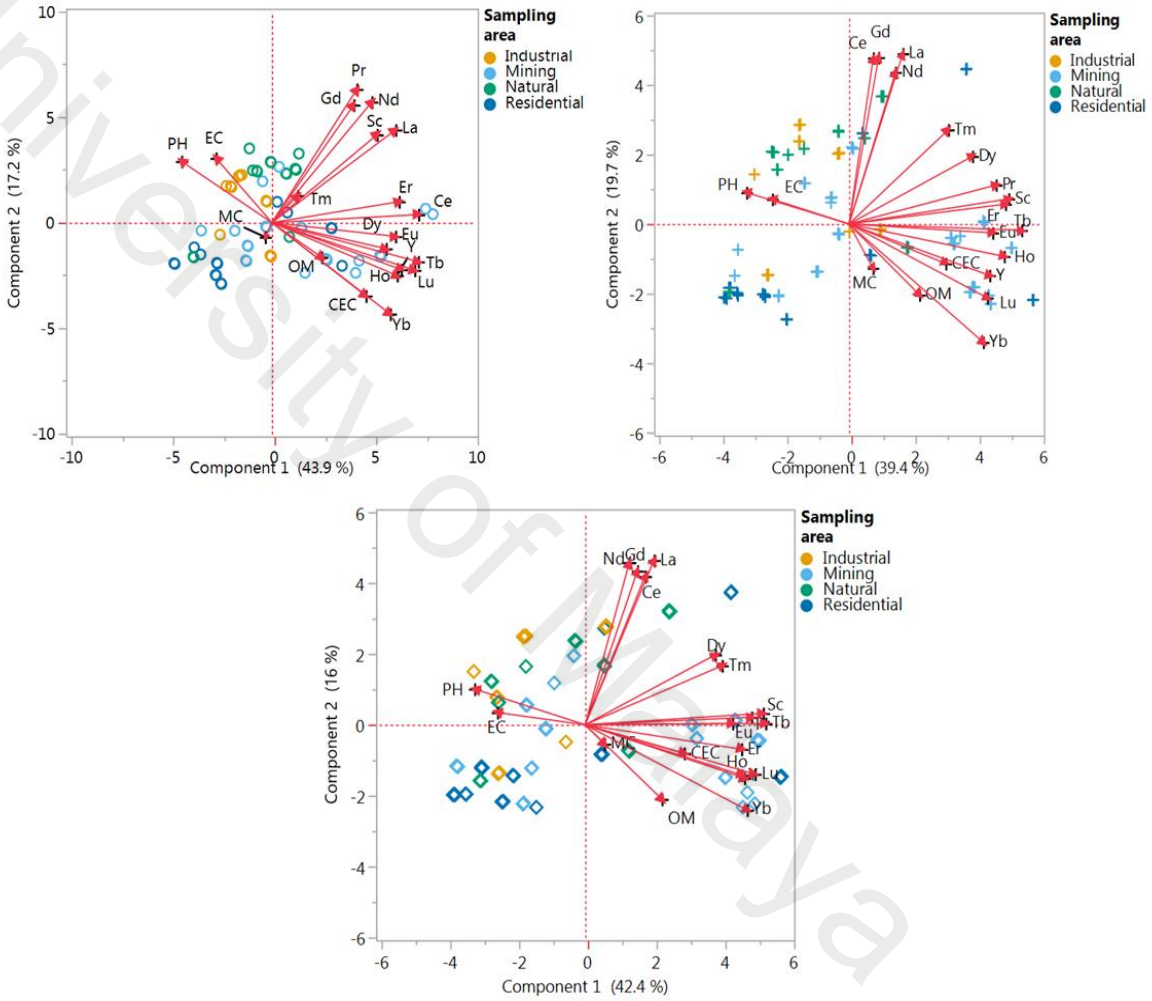


Figure 4.17: Biplot of soil samples from different soil depths based on areas (a) surface soil (b) middle soil (c) lower soil.

This means that PC1 is responsible for the separation of most soil samples within the 'mining' area from natural and industrial where PC2 causes the separation of most of the samples of the residential area from mining.

The soil samples from the 'mining' area located at the lower right hand side of the quadrant are loaded Er, Eu, Ce, Dy, Ho, Lu, Tb, Y, CEC, Yb and OM while those in the lower left hand side of the quadrant are depleted in Pr, Sc, Nd, Gd, La and Tm. MC is the dominant factor for the mining samples located at lower left of the quadrant. In surface soil (depth of 0-20 cm), most of the samples from mining area were enriched with REE elements of Er, Ce, Dy, Eu, Y, Tb, Lu, Ho, and Yb. Two physical parameters of OM and CEC are the discriminating factors for separation of most of the samples in mining area while MC is an important factor for the small number of soil samples in mining area. Rare elements were not noticed in samples from natural, industrial and residential areas and were found in samples of majority of mining areas.

Fig. 4.17 (b) biplot presents the separation of soil samples at the depth of 21-40 cm. PCA explains 59.1% of the total variance with five eigenvalues >1. As observed, the samples are generally clustered into four samples from each group although some samples are also seen to spread throughout the graph. Samples from the industrial area mostly have positive PC2 and are located in upper left quadrant of the graph loaded with pH and EC. Few of the industrial samples are located in lower left quadrant and are depleted with Gd, Ce, La, Nd. The mean concentration of rare elements and the values of physical parameters for middle soil (21-40 cm) is listed in **Table 4.15**.

Most of the samples from the 'natural' area are located at the upper half of the graph and their separation is due to the PC1 scores. Samples in this group are loaded in Ce, pH, Gd, La, Nd and Ec but depleted in Mc, Yb, Lu, OM, Y, Ho, and CEC. On the other hand, most samples in the 'residential' area are located at the lower left hand side of the

quadrant and have negative PC1 and PC2. The separation of samples in this group is based on both the PC1and PC2 scores. Samples in this group are depleted in Ce, La, Gd, Nd, Tm, Dy and Pr. Samples from the 'mining' area are spread in the second, third and fourth quadrant and are loaded by pH, EC , MC, Yb, OM, Lu, Ho, Y, CEC, Tb, Eu and Er. Overall in the middle soil layer (21-40 cm) rare elements were found in fewer samples of mining areas. Physical parameters of MC, OM and CEC are important in separation of most of the samples from mining areas. Separation of samples in residential area is only because of depletion of rare elements of Ce, Gd, La, Nd, Tm and Dy while MC is not the dominant factor in separating samples from residential area as it was in 0-20 cm layer.

Figure 4.17 (c) biplot illustrates the lower soil (41-60 cm) explaining 58.4 % of total variance with five eigenvalues >1. As observed, the samples are in general separated into four clusters although the spread of data is higher compared to the samples collected from the surface and middle soil. Most of the samples from the 'industrial' area have been found in positive PCI and PC2 and are loaded with pH and EC. Some of the samples in this group are located in upper right half of the graph and loaded with Nd, Gd, Dy, Tm and Ce.

Most of the samples from the 'natural' area are located at the upper half of the graph and are loaded with Ce, La, Gd, Nd and pH. PC1 scores are still responsible for the separation of most of the samples in this group from the other two areas. Samples from the 'residential' area are depleted in Ce, Gd, La, Dy, Tm and Nd while samples from the 'mining' area are more spread out in the second, third and fourth quadrants and loaded with Eu,Tb, Sc, Pr, Er, Y, Ho, Yb, Lu, pH and EC.

In general, it can conclude that comparing the distribution of rare elements and physical parameters for the different sampling depths does not affect the clustering of

samples. However, it can be noted that the samples are more spread out as we move from the surface soil to deeper soil although the loadings do not change much and the clustering is still clear. In other words, mapping the distribution of soil samples to four groups of 'mining', 'natural' and 'residential' and 'industrial' areas give similar information for the different depths confirming that the analysis of surface soil (0-20 cm) is sufficient for the current study except that moving from surface soil to middle and deeper soil as the samples spread out the number of samples in mining area being loaded with REE gets less and physical parameter of MC gets more dominant in samples of middle and bottom soil mining areas. The mean concentration of rare elements and the values of physical parameters for lower soil (41-60 cm) is listed in **Table 4.15**.

4.3.4 Environmental Risk Assessment

Average values of enrichment factor (EF), geoaccumulation index (Igeo), contamination factor (CF) and pollution load index (PLI) for the soil samples are shown in Table 4.16.

The calculated average EF values for all fourteen REEs except Sm and with Sc and Y in three depths of the soil samples listed in Table 4.16. The mean enrichment factors (EFs) of Sc, Er, Tm, Eu, Gd, Tb, Dy and Lu in surface soil (0-20 cm) were greater than 9, suggesting major effects from source such as non-crustal. Meanwhile, the EF values in lower soil depth (41-60 cm) found higher than deep soil (21-40 cm) suggesting that REEs are more deposited in complex mineral form. The mean values of EF ranged from 9.02 to 83.18 from surface to bottom layers for Sc, Er, Tm, Eu, Gd, Tb, Dy and Lu suggesting these elements also originated from anthropogenic sources. Such high values represent mining activities carried out long ago but their significances are still present. High EF values point towards more pollution.

Table 4.15: Mean values (mg kg^{-1}) of REEs in different areas of ex-mining with standard deviations.

Soil depth	Surface soil (0-20 cm) Average concentration				Middle soil (21-40 cm) Average concentration				Deeper soil (41-60 cm) Average concentration			
Areas	Industrial area	Mining area	Natural area	Residential area	Industrial area	Mining area	Natural area	Residential area	Industrial area	Mining area	Natural area	Residential area
pH	6.38 ± 1.42	5.9 ± 0.88	6.65 ± 1.11	6.10 ± 0.96	6.52 ± 1.40	5.48 ± 1.42	6.77 ± 0.72	6.03 ± 0.48	6.43 ± 1.28	5.45 ± 1.69	6.84 ± 2.06	5.96 ± 1.35
EC	75.18 ± 4.51	22.25 ± 1.64	99.16 ± 6.59	58.21 ± 2.55	75.23 ± 5.95	34.56 ± 5.88	107.4± 8.27	45.31 ± 4.95	77.39 ± 5.91	25.30 ± 2.08	108.8 ± 12.77	47.06 ± 4.18
CEC	14.74 ± 4.88	19.42 ± 3.56	12.80 ± 2.47	18.72 ± 4.55	14.22 ± 3.95	20.22 ± 2.95	13.24 ± 1.15	18.23 ± 2.77	15.07 ± 1.45	20.14 ± 1.11	13.15 ± 1.58	18.13 ± 2.44
OM	11.72 ± 3.21	12.79 ± 2.25	12.67 ± 4.45	15.25 ± 5.58	12.81 ± 4.75	15.51 ± 3.49	14.15 ± 1.09	16.64 ± 3.15	14.32 ± 2.55	16.47 ± 2.75	14.40 ± 2.29	16.41 ± 2.23
MC	26.38 ± 2.55	23.73 ± 3.81	18.26 ± 3.66	20.31 ± 2.84	27.90 ± 6.71	25.93 ± 4.88	20.83 ± 2.55	21.58 ± 2.96	29.24 ± 3.18	26.49 ± 4.55	22.29 ± 1.75	21.70 ± 3.95
Sc	25.94 ± 5.82	35.63 ± 1.25	38.15 ± 6.81	22.65 ± 7.25	19.12 ± 3.17	22.65 ± 6.15	17.68 ± 3.63	15.38 ± 3.35	14.57 ± 4.48	20.51 ± 3.44	16.36 ± 4.57	14.72 ± 3.78
Y	26.30 ± 2.55	50.1 ± 5.58	30.09 ± 3.96	34.88 ± 6.34	23.83 ± 5.85	39.83 ± 4.14	23.34 ± 1.52	26.41 ± 4.55	15.54 ± 2.88	35.72 ± 4.66	19.59 ± 3.12	24.57 ± 3.41
La	42.79 ± 3.71	51.97 ± 2.83	53.63 ± 2.87	33.39 ± 5.78	28.06 ± 4.33	23.97 ± 3.02	36.28 ± 4.17	23.30 ± 1.44	27.88 ± 6.39	20.85 ± 3.12	30.84 ± 7.08	22.65 ± 5.58
Ce	63.54 ± 6.22	90.61 ± 4.22	73.47 ± 7.20	61.20 ± 5.33	46.98 ± 4.15	35.97 ± 4.74	55.36 ± 6.12	36.69 ± 1.82	35.55 ± 4.98	30.83 ± 4.27	43.48 ± 6.27	34.53 ± 5.75
Pr	19.99 ± 4.76	19.78 ± 4.50	27.55 ± 6.32	11.04 ± 3.32	7.43 ± 1.08	10.49 ± 1.33	11.37 ± 2.10	7.39 ± 1.01	4.77 ± 1.08	8.80 ± 1.11	8.27 ± 1.31	6.84 ± 1.24
Nd	87.17 ± 1.81	66.23 ± 1.19	76.85 ± 5.56	41.70 ± 3.23	39.94 ± 4.40	34.46 ± 2.85	43.36 ± 5.24	25.98 ± 4.04	39.82 ± 6.15	30.32 ± 1.24	35.62 ± 5.58	24.47 ± 6.15
Eu	3.16 ± 5.33	8.43 ± 3.70	6.04 ± 1.02	6.11 ± 2.05	2.70 ± 0.75	5.66 ± 1.72	3.64 ± 1.11	4.34 ± 0.76	1.87 ± 1.05	4.47 ± 1.02	2.84 ± 0.55	4.03 ± 0.58
Gd	32.37 ± 4.25	25.58 ± 3.62	28.37 ± 2.55	15.55 ± 2.17	17.54 ± 2.01	13.62 ± 2.93	14.62 ± 3.44	9.37 ± 1.11	14.12 ± 2.44	10.54 ± 1.55	10.73 ± 1.63	8.44 ± 1.33
Tb	13.93 ± 1.41	24.16 ± 4.96	14.06 ± 4.85	14.84 ± 3.39	10.49 ± 1.36	17.09 ± 3.35	10.76 ± 1.15	9.11 ± 1.55	7.29 ± 1.11	15.39 ± 3.45	8.91 ± 1.91	8.27 ± 1.25
Dy	11.67 ± 3.15	20.1 ± 6.84	14.33 ± 2.15	12.01 ± 1.52	8.50 ± 2.55	11.41 ± 2.22	10.99 ± 3.55	8.19 ± 2.44	6.63 ± 1.33	8.91 ± 1.58	9.56 ± 1.44	6.99 ± 1.18
Ho	1.49 ± 0.86	5.78 ± 1.52	3.06 ± 0.57	4.59 ± 1.12	1.71 ± 0.95	3.62 ± 1.11	2.30 ± 0.25	2.61 ± 0.84	0.91 ± 0.18	3.77 ± 1.11	1.87 ± 0.63	2.41 ± 0.66
Er	7.75 ± 1.17	13.46 ± 2.70	7.45 ± 1.59	5.66 ± 0.86	4.98 ± 2.17	5.45 ± 0.88	3.55 ± 1.08	3.39 ± 0.77	3.60 ± 1.14	5.86 ± 1.07	3.38 ± 1.00	3.44 ± 1.15
Tm	9.49 ± 2.24	9.67 ± 2.51	14.90 ± 4.34	6.07 ± 1.75	5.40 ± 1.04	5.46 ± 1.28	5.60 ± 1.32	3.70 ± 0.44	4.02 ± 0.66	4.44 ± 0.88	4.06 ± 0.75	3.23 ± 0.85
Yb	9.59 ± 1.46	22.92 ± 3.99	8.91 ± 2.88	15.02 ± 2.69	7.23 ± 1.99	16.68 ± 1.77	5.36 ± 1.19	10.93 ± 1.55	3.92 ± 0.77	14.06 ± 2.89	5.30 ± 0.34	10.56 ± 2.44
Lu	1.33 ± 0.23	4.49 ± 1.28	2.04 ± 1.87	2.17 ± 0.88	0.76 ± 0.25	3.18 ± 1.08	1.37 ± 0.63	1.57 ± 1.01	0.61 ± 0.15	3.11 ± 0.69	1.58 ± 0.49	1.65 ± 0.22

REEs stored in profiles comes from different rocks, including carbonate, sillicalite and shale were determined by various methods and enrichment properties of soil. Grayish black carbonaceous mudstone in China was found highly enriched with REEs. ΣREE contents ranged from 89.0 to 9965 mg kg^{-1} with a mean value of 1312 mg kg^{-1} (Zhang et al., 2016).

Both Tm and Tb have the highest enrichment in certain locations in surface soil (0-20 cm) exceeding the concentration of all locations. For Tm has very severe enrichment factor which it's average EF is 61.65 while Tb has a high EF with the average value of 57.39 in surface soil. Yb, Gd, Eu, Er and Ho show severe enrichment in the upper soil surface. Sc, Pr, Nd, and Dy are moderately enriched while Ce, Y and La fall in the category having minor enrichment.

In the deep soil (21-40 cm) Tb and Tm have higher EF average values with 48.35 and 43.29 meaning that Tb increasing with depth, showing very severe enrichment. Yb and Lu show severe enrichment while the rest of REEs has moderately severe to minor enrichment in this soil depth profile. Deeper into the soils (41-60 cm), enrichment factor increases for all REEs compared to subsoil surface. Tb and Tm show average enrichment factor of 83.18 and 71.77 respectively. Average values of Yb and Lu varies as 26.61 and 36.05 while average EF values for Eu, Gd, Dy, Ho, and Er are 19.1, 14.42, 11.31, 16.44 and 10.32 respectively. Y, Sc, La, Ce, Pr, and Nd show minor to moderately enrichment factor with average values 7.07, 2.79, 4.27, 3.01, 5.71 and 6.32 respectively. Such distribution may be related to many sources of pollution mainly focusing on mining in that area, agriculture, and expansion of tin mining anthropogenic activities in the area (Liang et al., 2014).

Table 4.16: Enrichment factor (EF), geoaccumulation index (I geo) values, contamination factor (CF) and pollution load index (PLI) of soil in different depths.

Parameters	Depth cm	Sc	Y	La	Ce	Pr	Nd	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
(EF)	0-20	9.93	4.25	3.31	2.66	6.03	5.19	14.37	13.83	57.39	8.83	11.23	9.02	61.65	17.98	20.59
	21-40	2.68	4.06	3.49	2.12	4.27	3.73	8.57	9.02	48.35	7.14	9.01	5.31	43.29	13.64	14.27
	41-60	2.79	7.07	4.27	3.01	5.71	6.32	19.1	14.42	83.18	11.31	16.44	10.32	71.77	26.61	36.05
I (geo)	0-20	11.4	10.15	9.78	9.54	10.51	10.41	11.76	11.79	13.87	11.17	11.25	11.02	13.98	12.08	12.21
	21-40	9.31	9.78	9.36	8.89	9.86	9.73	10.83	11.04	13.36	10.62	10.83	10.18	13.32	11.3	11.46
	41-60	8.74	9.46	8.83	8.25	9.22	9.45	10.91	10.65	13.11	10.26	10.61	9.88	13	11.19	11.52
CF	0-20	4.46	1.91	1.49	1.19	2.7	2.33	6.45	6.2	25.75	3.96	5.04	4.04	27.66	8.07	9.24
	21-40	1.02	1.54	1.13	0.79	1.62	1.42	3.18	3.34	18.37	2.71	3.42	2.02	16.04	5.18	5.42
	41-60	0.69	1.31	1.47	0.56	1.06	1.17	3.53	2.67	15.39	2.09	3.04	1.86	13.28	4.92	6.67
PLI	0-20 cm			4.4		21-40 cm			2.54		41-60 cm			2.31		

These results describe extant evidence of ex-tin mining sites in Kinta district, especially in the Lahat, Kampar, Batu Gajah, Taman Bukit Merah, Menglembu and Kota Bharu areas. Average I*geo* values show elevated amounts of REEs in the soil, suggesting area heavily polluted.

Results appear to be in last category having values greater than 5 indicating severely polluted with rare earth where *Cn* is the concentration of the element in the sample and *Bn* is the background value of the element based on (Gao et al., 1998). Almost all REEs are mostly accumulated in the upper soil surface and decrease with depth. This area already nominated as hazardous by Akif et al. 2014.

Summary

This chapter detailed out the physico-chemical parameters of REEs in water, sediments and soil. Microwave acid digestion method was used to digest the sample and analyzed using ICP-MS. Concentration of REEs in water, sediment and soil has been found and toxicity has also been identified. Data obtained in analytical results has been identified by statistical analysis such as factor analysis (FA), principal component analysis (PCA) and Hierarchical component analysis (HCA). Environment impact assessment has been done using different environmental factors such as enrichment factor (EF), geoaccumulation index (Igeo), contamination factor (CF) and pollution load index (PLI). The study confirms the presence and distribution of REEs in different samples collected from the study area and pollution impacts on the environment.

CHAPTER 5: SPECIATION STUDY OF SEDIMENTS AND SOIL

In this study based on the research, speciation of REEs using sequential extraction procedure has been done. Sediment and soil samples were collected from the ex-mining area for speciation study. Sediment samples were taken from ex-mining lake while soil samples were collected throughout the area from three different depths at each sampling station. REEs speciation study gives a better understanding of the contamination scenario in sediment/soil.

5.1 REEs speciation and mobility in sediment using sequential extraction procedures

Relative standard deviation obtained from replicate samples of mining lake sediments demonstrate REEs in good agreement. Results of sequential extraction procedure are presented in **Table 5.1** and **Figure 5.1** along with the determination of the total content of particular REEs in the samples studied and the percentage of the five fractions distinguished. Variations in the results after fractionation have been found for REEs as given in **Table 5.1**.

Analysis of the data obtained showed that REEs occurred mainly in the adsorbed/exchangeable/carbonate fraction (45 %) and in the form bound to silicates/residuals (32 %), and in much smaller amounts in the form of sulphides/organics (22 %). Only minor amounts of REEs were detected in the Fe oxides (13 %).

Scandium (Sc) is present about 35.4% in adsorbed/ exchangeable/carbonate (AEC) and about 32 % in silicates and residual oxides which is the highest of all the REEs. The greater percentage of Sc in the residual fraction indicates less pollution. Very small percentage of Sc of 8.2 %, 7.3 %, and 17.1 % was found in amorphous, crystalline Fe oxyhydroxides and sulphides and organics respectively. Such differentiation reflects the

deposition of Sc on the surface of sediments in the form of carbonates. Yttrium (Y) shows a maximum of 46.2 % in AEC phase in all REEs but less in other fractions. Perak morphologically is famous for its tin mining operation represents both original and anthropogenic origin of yttrium in the sediment samples (Ong et al., 2015).

Lanthanum (La) being second most REE in AEC phase after Y but the highest in silicates and residual oxides (41.1%). Monazite mineral used for extraction of REEs in tin mining operation in the study area clearly indicate anthropogenic origin of this element. La could be released from REO while carbonates leach REEs under acidic conditions. Cerium (Ce) shows 39.0 % and 30.7 % in AEC and silicates and residual oxides respectively. This is also a chief element of tin bearing mineral.

Praseodymium (Pr) shows much variation in its percentage fractions, but more uniformly distributed in all sediment fractions than other REEs. Pr found distributed with 39.3 %, 10.7 %, 9.7 %, 16.0 % and 24.3 % in all the five fractions of sequential extraction procedure. Neodymium (Nd) shows relatively 36.1 % in AEC fraction, but less in bound to sulphides and organics (19.4 %). Some distinct part also found in crystalline Fe oxyhydroxides. Many rocks found on the upper side of lake rich in Fe making different layers were seen clearly. Such rocks were found red and yellow in colour with iron bearing minerals, meaning that REEs could also be associated with these minerals along with tin bearing minerals. Heavy rainfall, acidic rain, erosion, weathering processes and natural disasters cause the damage to these rocks resulting in spreading of REEs into the lakes, reservoirs, rivers, oceans and all around the terrestrial and aquatic ecosystem.

Table 5.1: Speciation analysis of sediments using five step sequential extraction procedures and potential mobility (%).

Metals	Fractions					Total concentration (mg kg^{-1})	Potential Mobility (%age)
	Adsorbed/Exchangeable/ Carbonates. (AEC) mg kg^{-1}	Bound to Amorphous Fe oxyhydroxide mg kg^{-1}	Bound to Crystalline Fe oxide mg kg^{-1}	Bound to Sulphides and Organics mg kg^{-1}	Bound to Silicates and Residual Oxides mg kg^{-1}		
Sc	35.54 ± 0.15	8.2 ± 0.09	7.3 ± 0.04	17.1 ± 0.46	32.0 ± 0.11	404 ± 1.22	50.9
Y	46.24 ± 0.08	8.6 ± 0.22	5.5 ± 0.16	12.3 ± 0.13	27.3 ± 0.22	852 ± 0.11	60.3
La	44.2 ± 0.29	2.8 ± 0.21	2.8 ± 0.11	9.1 ± 0.25	41.1 ± 0.19	7658 ± 0.22	49.8
Ce	39 ± 0.24	5.4 ± 0.18	5.5 ± 0.28	19.3 ± 0.17	30.7 ± 0.15	1723 ± 1.15	50.0
Pr	39.3 ± 0.11	10.6 ± 0.04	9.7 ± 0.06	16 ± 0.11	24.3 ± 0.18	460 ± 0.55	59.7
Nd	36.1 ± 0.15	8.9 ± 0.26	9.3 ± 0.17	19.2 ± 0.28	26.5 ± 0.08	364± 0.15	54.3
Eu	39.6 ± 0.08	7.2 ± 0.02	8.0 ± 0.11	19.4 ± 0.05	25.8 ± 0.07	156 ± 0.12	54.8
Gd	41.8 ± 0.11	11 ± 0.29	9.4 ± 1.12	13.4 ± 0.26	24.4 ± 0.22	625± 0.33	62.2
Tb	29.2 ± 0.05	11.7 ± 0.01	12.7 ± 0.11	19.3 ± 0.16	27.0 ± 0.03	47.8± 0.05	53.7
Dy	39.5 ± 0.23	11.2 ± 0.15	9.6 ± 0.20	15.4 ± 0.28	24.3 ± 0.25	882± 1.11	60.3
Ho	29.7 ± 0.36	11.7 ± 0.22	9.9 ± 0.25	22.9 ± 0.11	25.8 ± 0.21	98 ± 0.11	51.3
Er	38.1 ± 0.24	12.3 ± 0.19	9.1 ± 0.27	17 ± 0.17	23.5 ± 0.13	282 ± 0.17	59.4
Tm	34.2 ± 0.12	13.1 ± 0.08	9.5 ± 0.15	19.4 ± 0.1	23.7 ± 0.24	181± 0.23	56.9
Yb	44.7 ± 0.23	12.7 ± 0.14	9.9 ± 0.33	15.4 ± 0.21	17.4 ± 0.18	261 ± 0.11	67.3
Lu	28.5 ± 0.17	12.7 ± 0.11	9.2 ± 0.16	21.1 ± 0.11	28.5 ± 0.17	159± 0.33	50.4

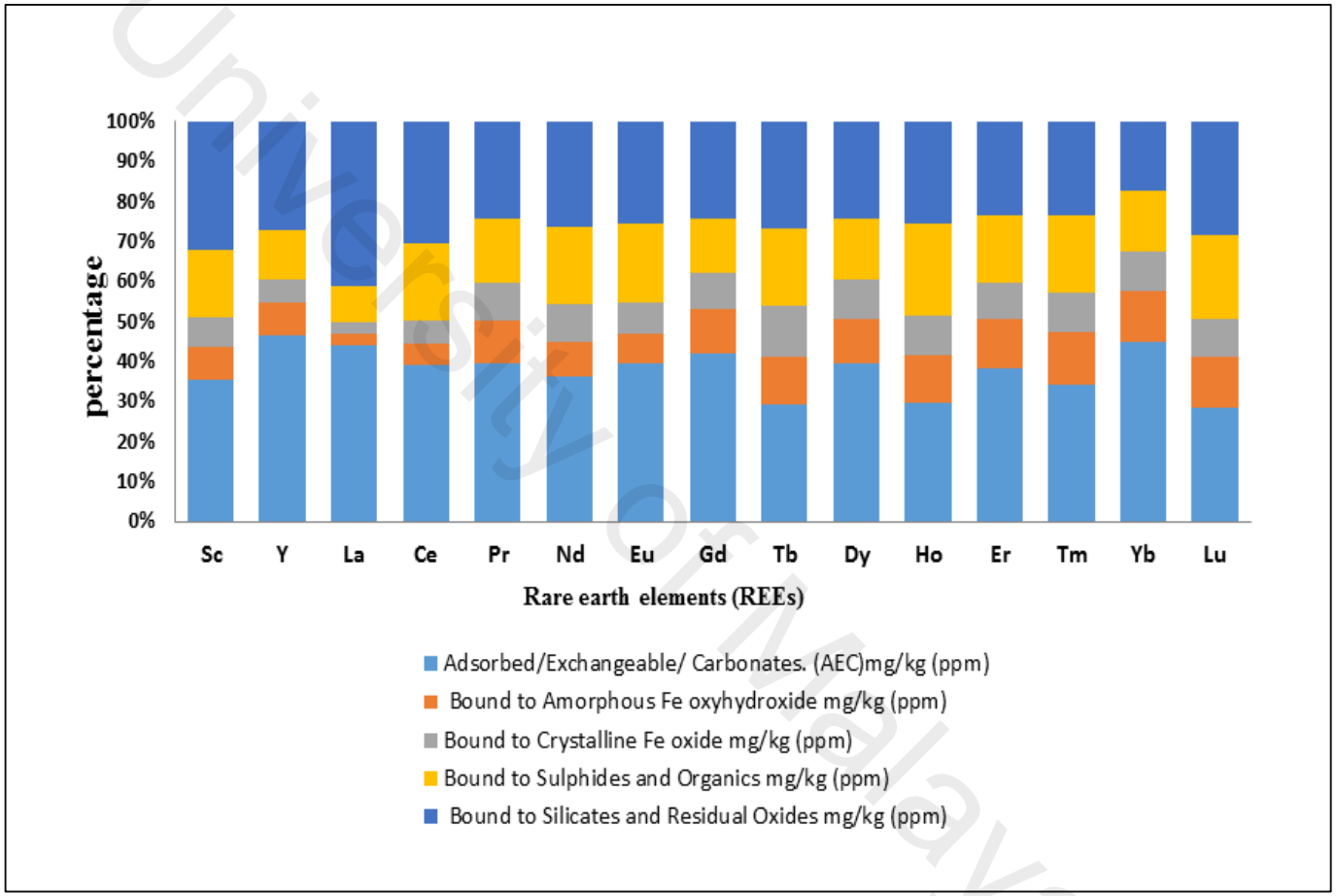


Figure 5.1: Fractional distribution of REEs in sediments.

Heavy rainfall, acidic rain, erosion, weathering processes and natural disasters cause the damage to these rocks resulting in spreading of REEs into the lakes, reservoirs, rivers, oceans and all around the terrestrial and aquatic ecosystem. From the speciation study, Euphorbium (Eu) show quite similar distribution with Ce in sequential extraction procedure. This trace element found maximum (39.6 %) in AEC fraction. Gadolinium (Gd) shows 41.8 % in fraction I and 11.0 % in amorphous Fe oxyhydroxides fraction which is higher than other previous rare earth elements. Terbium (Tb) found almost equally distributed in all fractions of the extraction procedure. This refers to enhanced danger and pollution because of application in different technologies. So it can conclude that occurrence of Tb could be because of anthropogenic origin.

Dysprosium (Dy) found 39.5 % in AEC fraction and 24.3 % in bound to silicates and residual oxides. Such percent distribution refers to anthropogenic origin in the mining lake sediments. Holmium (Ho) found only rare earth in sediments with a maximum distribution percentage of about 22.9 in bound to sulphides and organic fraction. This indicates the presence of compounds of sulphur and organic material deposit onto the sediment surface. Erbium (Er) found in higher amount in fraction I while thulium (Tm) shows the highest percentage of 13.1 in amorphous Fe oxyhydroxides fraction in nearly all sediment samples. REEs usually acts as a main barrier, cement and nodule present in oxide form among particles. Such REO become mobile if conditions become acidic even REEs organic phase because of organic matter also become mobilized under such conditions (Huang et al., 2007).

Ytterbium (Yb) shows 44.7 %, 12.7 %, 9.9 %, 19.4 % and 23.7 % in all five fractions respectively. The main source of ytterbium is related to the mining activities, land use changes and some of the anthropogenic activities (Long et al., 2012). Leutetium (Lu) found second maximum rare earth in sediment samples with 21.1 % in sulphides and

organic fraction. The REEs degree of pollution is measured by residual fractions. More REEs represents less pollution index.

Overall results indicate REEs potentially more available for exchange and/or release into the aquatic environment was found in the adsorbed/ exchangeable/carbonate fraction and residual fraction, the most chemically recalcitrant and least bioavailable in sediments. Anthropogenic REEs extracted during the first step of sequential extraction while lithogenic REEs were more present in the residual fraction (Martins et al., 2013).

Speciation study basically gives information about the potential mobility of trace elements. Sum of concentrations of the REEs in different media indicate potential mobility (Ashraf et al., 2011). The potential mobility of all rare earths is obtained by taking the sum of AEC, amorphous Fe oxy, Cry Fe oxy, bound to sulphides and organics and silicates and residual phase of that rare earth element (Huang et al., 2007). As depicted from **Table 5.1** and **Figure 5.2**, it can be considered that maximum potential mobility is for Yb (67.3 %), Gd (62.2 %) and then Dy (60.3 %) and Y (60.3 %) show same potential mobility in sediments.

The main source for their mobility may be the minerals and the complex ions adsorbed on the surface of sediments. REEs mobility and bioavailability is dependent on exchangeable phase and easily available to the environment. Pr (59.7 %), Er (59.4 %), Tm (56.9 %), Eu (54.8 %) and Nd (54.3%) show about similar potential mobility while Sc (50.9 %), La (49.8 %), Ce (50.0 %), Ho (51.3 %) and Lu (50.4 %) show similar trends in sediment fractions.

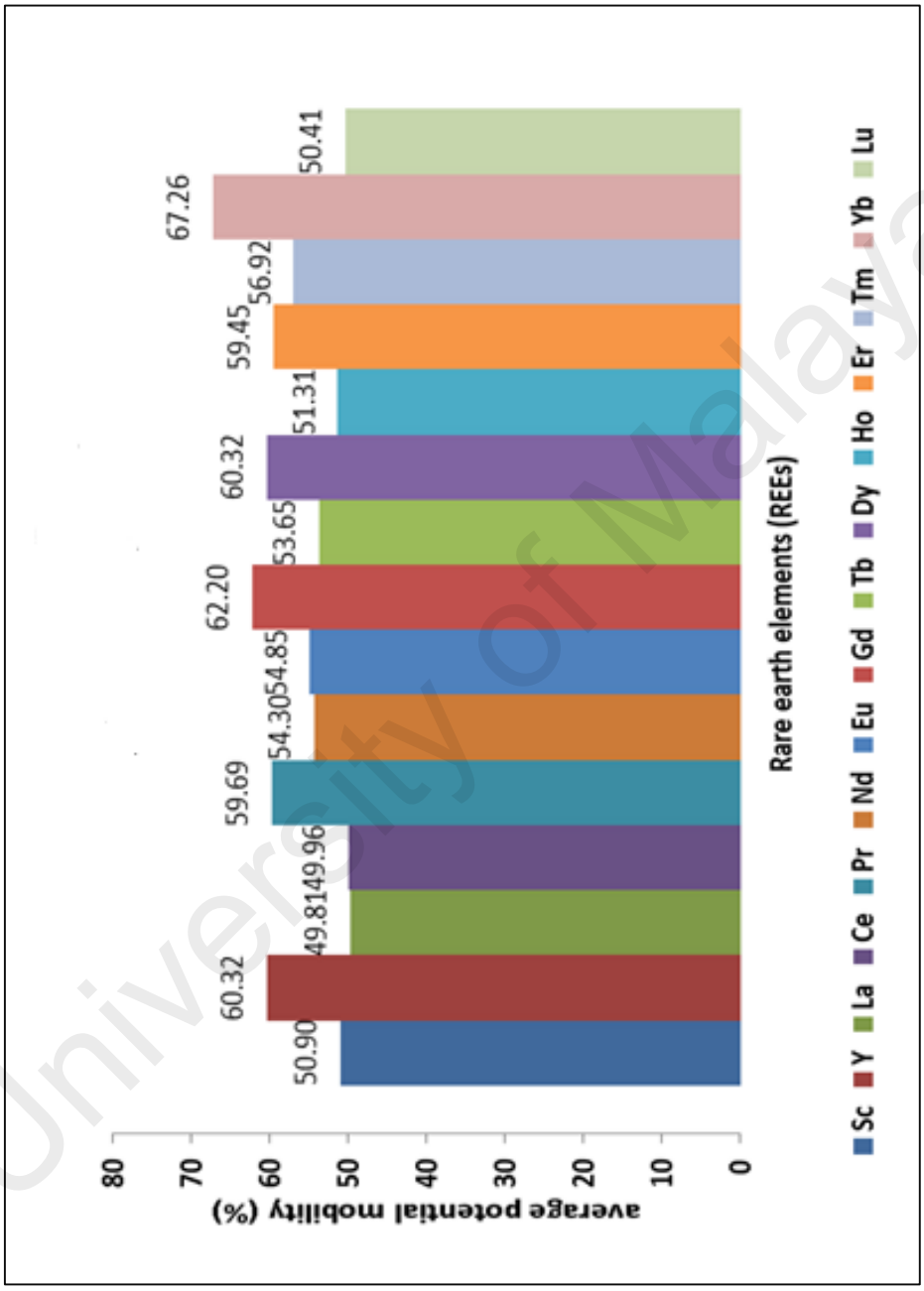


Figure 5.2: Potential mobility (%) of REEs in sediments.

Higher percentage of silicates and organics present in sediments indicate more oxidizing capacities of REEs in the aquatic environment. REEs mobility vary in the following order: Adsorbed/exchangeable/carbonates > silicates and residual bound > sulphides and organics bound > bound to Fe oxyhydroxides (amorphous) > bound to Fe oxyhydroxides (crystalline).

There are many factors that control the mobility of REEs in aquatic ecosystems. Such factors may include pH, climatic conditions, weathering, nature of the rocks (igneous) bearing REEs in the vicinity of water body, dissolution, solubility, ionic radius, dissolved ionic species, alluvial deposits and adsorption capacity (Davranche et al., 2015). pH is considered as important in REE mobility. Absorption of rare earth elements (REEs) increases with increase in pH which ultimately decrease its mobility. Absorption and removal of REEs from water depend on the coagulation and precipitation of Fe-Al- Mn oxyhydroxides on the surface of sediments. In water bodies pH also controls the behaviour of REEs by their presence and total concentration. Potential mobility of REEs in soluble fractions of speciation can also be determined by their total load in suspended and sediment condition transferred to river or lake waters. Areas with massive igneous rocks have more potential for REs mobility by dissolution in water body. A previous study conducted by Martins et al (2013) also demonstrates higher potential mobility of HREEs than LREEs due to their ionic strength and low bonding capacities.

In the current study, concentration of Ce, La, Nd, Sc and Y is higher with average values (ppm) 67.21, 337.85, 13.1, 14.2, 39.47 in adsorbed/exchangeable/carbonate fraction and 33.19, 69.33, 6.98, 6.86, 10.52 in organic fraction and 52.99, 314.5, 9.61, 12.87 and 23.47 in residual fraction respectively. Martins et al (2013) also present concentration of sediments in sequential extraction procedure show Ce, La, Nd, Sc and

Y with average concentration (ppm) 1.327, 0.414. 0.681, 0.902 and 0.068 respectively in AEC fraction.

A previous study conducted by Kato et al (2011) in east south and central north Pacific Ocean describe sediments as potential REEs and yttrium oxides source (9,110 ± 1,460 tonnes) producing 25000 ± 4000 tonnes of REY oxides competing annual consumption (Kato et al., 2011) while in the current study REEs ranged from 9-800 mg kg^{-1} in the sediments.

Sequential extraction Indicate neodymium concentration in sediments (3.7 to 10.1 ppm) which was found less than upper continental crust value for Nd (Willis & Johannesson, 2011). In this study, Nd in all sediment samples ranged up to 38.7 mg kg^{-1} which is much higher than compared to Willis and Johannesson, (2011). Nd found more bound in adsorbed/ exchanged/ carbonate fractions and then in silicates and residues. This suggests silica nature of sediments and preferring source of REEs to mining lake water may be dissolution of carbonate from limestone rocks in the mining area and after mining water sediments found rich in REEs minerals.

This study also gives ratio of REEs from light to heavy (L/H) ranging from 4.87 ± 1.46 to 765.8 ± 3.66. Higher contents of LREEs were found in the sediment samples compared to the study Liu et al. 2011 which show REEs in two lacustrine sediment cores in the maritime Antarctic with relative to concentrations of REEs illustrate intense variations (Liu et al., 2011). This indicates higher deposition of REEs onto the sediment surface.

5.2 Speciation study of soil

Determining the total REEs concentration in the soil through acid digestion does not provide complete information about their ecotoxicity and potential mobility in the environment. Toxicity of the REEs largely depends on the form in which they are bound

to different components and distributed in the soil (Aikpokpodion et al., 2013). A chemical speciation is a unique tool in understanding the REEs chemical form, potential mobility, bioavailability as well as transformation under suitable conditions to other environmental compartments such as from soil to water, plants and human beings (Barkouch and Pineau, 2015). It follows a five-step procedure proposed by Hall et al. (1996). Speciation identifies sources of metal pollution in the soil environment. REEs which are extracted in the first step of extraction procedure are due to anthropogenic activities while in the last step of extraction (silicate and residual fraction) signifies lithogenic origin (Todorović et al., 2014).

REEs speciation in three different depths in soil shows much variation. It is considered important for the potential mobility and bioavailability of REEs in ex-mining soil. Mean values of REEs in five steps sequential extraction procedure carried out for speciation are listed **(Appendix E),** where distribution of major species is represented as mg kg^{-1} and percentage in **Table 5.2** of total REEs dissolved content.

Potential mobility of the REEs indicates their abundance in different soil depths and is described as bound to silicates and residuals > bound to adsorbed/exchanged/carbonates > bound to sulphides and organic > bound to crystalline Fe oxyhydroxides > bound to amorphous Fe oxyhydroxides. This trend continues to be same with soil depth, but some variations have been seen.

Table 5.2: Percentage fractional analysis and potential mobility for REEs in sequential extraction procedures for different soil depths.

Metals	Fractions (%) in (0-20 cm) soil depth					Total concentration (mg kg^{-1})	Potential Mobility (%)
	Fraction I	Fraction II	Fraction III	Fraction IV	Fraction V		
Sc	9.31	5.04	5.14	9.68	10.17	661.68	49.54
Y	16.54	6.09	6.75	13.00	16.57	872.22	49.83
La	11.21	5.02	4.63	21.54	19.50	897.39	33.69
Ce	17.18	6.35	5.98	48.15	32.08	1370.15	26.89
Pr	3.68	1.93	2.10	8.84	6.83	502.28	32.97
Nd	12.26	4.83	4.48	33.63	23.84	1032.58	27.28
Eu	3.26	0.91	0.45	2.40	4.54	390.76	39.96
Gd	3.80	1.70	1.69	13.03	8.32	549.83	25.19
Tb	7.77	2.91	2.56	5.95	10.18	578.09	45.08
Dy	5.36	1.80	1.94	6.56	8.15	511.21	38.21
Ho	1.90	0.57	0.34	2.89	2.91	363.95	32.63
Er	3.23	0.92	0.63	6.64	5.84	438.37	27.69
Tm	3.24	0.62	0.66	2.31	4.07	383.79	41.46
Yb	6.70	2.44	1.91	7.87	7.98	541.91	41.07
Lu	1.69	0.27	0.31	1.79	2.14	335.49	36.60
REEs in (21-40) cm soil depth							
Sc	4.01	2.60	2.83	7.47	9.25	264.70	36.08
Y	7.63	3.75	3.63	17.66	16.44	495.20	57.37
La	6.59	2.88	3.26	10.06	10.25	333.60	93.46
Ce	7.08	3.33	3.26	15.16	57.00	439.60	52.25
Pr	3.18	1.61	1.71	4.55	3.43	145.50	24.84
Nd	6.58	3.86	3.19	11.34	9.32	353.40	77.10
Eu	2.01	0.95	0.72	2.18	2.46	85.40	14.06
Gd	2.73	1.06	3.44	4.03	4.08	131.10	27.63
Tb	4.58	1.95	1.59	6.01	6.83	216.10	41.70
Dy	3.24	1.5	1.01	4.38	5.28	160.00	21.98
Ho	0.81	0.52	0.4	1.54	1.68	50.30	6.61
Er	1.21	0.47	0.39	2.00	1.68	66.00	36.00
Tm	1.35	0.65	0.51	1.56	2.00	62.10	9.59
Yb	6.03	1.97	1.54	5.61	7.10	204.90	36.46
Lu	0.83	0.44	0.28	1.64	1.97	46.10	46.06
REEs in (41-60 cm) soil depth							
Sc	3.80	3.14	2.22	7.31	9.22	252.81	35.65
Y	7.30	3.24	3.27	16.90	16.23	474.89	29.42
La	6.32	2.51	2.64	9.44	9.75	308.71	37.41
Ce	6.37	2.83	3.03	14.37	14.01	413.95	30.11
Pr	2.92	1.35	1.32	4.12	2.98	129.32	44.05
Nd	6.14	3.16	2.52	9.66	8.64	319.58	39.24
Eu	1.72	0.65	0.57	1.68	1.96	69.44	44.68
Gd	2.15	0.84	0.82	3.30	3.51	109.28	35.87
Tb	4.01	1.47	1.21	5.24	6.10	187.37	37.10
Dy	2.59	1.17	0.80	3.21	3.64	121.23	39.96
Ho	0.89	0.41	0.30	1.35	1.54	46.09	35.63
Er	1.90	0.85	0.68	2.30	2.66	84.84	40.88
Tm	1.18	0.51	0.40	1.23	1.93	53.65	39.80
Yb	5.40	1.55	1.37	6.15	7.10	201.08	38.57
Lu	0.76	0.32	0.22	1.43	1.72	45.29	29.21

It can be concluded that there is no specific correlation in the soils solution and solid phases, but dissolution or distribution of REEs is more correlated with acid extract solutions (Palumbo-Roe et al., 2015).

Adsorbed/exchanged/carbonates (AEC) fraction (FI) contains REEs that can be released, precipitated or co-precipitated with carbonate contents of the soil. Among all fractions of sequential extraction, fraction I determines the potential mobility and bioavailability of REEs in contaminated sites of the study area (Huang et al., 2013b). Fraction I in the surface soil (0-20 cm) show electrostatically bound rare earth elements (REEs) that have been adsorbed on the soil surface and can be easily released, exchanged, precipitated or bound to the carbonate fractions present in the soil. Ce was found in highest percentage of 17.18 % along with Y, Nd, La and Sc having 16.54 %, 12.26 %, 11.21 % and 9.31 %, respectively as shown in **Figure 5.3 (a)**.

Presence of REEs more in the FI fraction (AEC) represents more availability of REEs and become a significant source of hazardous pollution in the environment (Ashraf et al., 2012). In China especially with mining activities, exchangeable REEs fractions being predominant forms in the soil (Yu et al., 2009, Zhang et al., 2012). In subsoil depth (21-40 cm) described in **Figure 5.3 (b)**, Y was found in the highest percentage (7.63 %) while Lu found lowest (0.83 %). Ce decreased in percentage up to 7.08 % compared to surface soil. Yttrium is considered as the main component in monazite ore for REEs refining and processing. La reach up to 6.59 %, Nd show 6.58 %, Yb was 6.03 % and Sc found much less in 4.01 %.

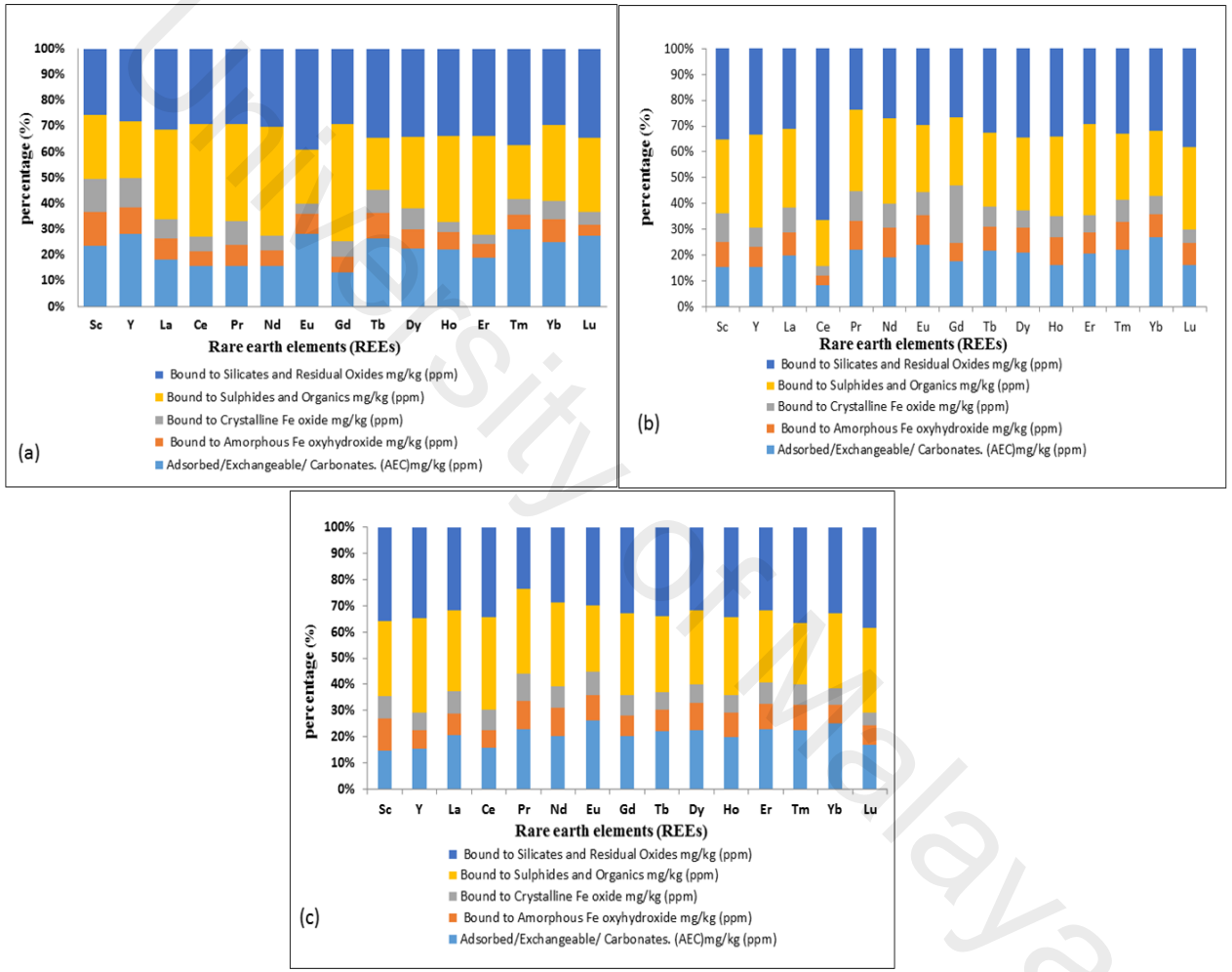


Figure 5.3: Relative distribution of REEs in different fractions of soil studied in three different depths (a) fractional distribution of REEs in surface soil (b) middle soil (c) deeper soil

A third layer of soil (41-60 cm) follow the same order of variation as second, but with fewer percentages for all the REEs shown in **Figure 5.3 (c)**. This is also considered as a valuable tool for mineral exploration in the soils and most abundant fractions in clayey fractions (Mongelli et al., 2014). It is demonstrated that most of the soil with each depth is rich in LREEs compared to HREEs. It can also be concluded that Fraction I (adsorbed/exchangeable/carbonates) constitute labile fractions and sources of REEs with Y and Ce being the most mobile and toxic in the environment compared to other metals (Filgueiras et al., 2004). Usually of total REEs, the 10 % average amount is present in AEC fraction of the soil (Wang et al., 2001b).

For REEs, fraction II (Amorphous Fe oxyhydroxides) and fraction III (crystalline Fe oxyhydroxides) show very little amount present. Ce and Y mostly bound in fraction II and III with 6.35 % and 6.75 % respectively. LREEs range from 1.69- 6.75 while HREEs ranged from 0.27- 2.91% in both fractions. This means that very few Fe bound REE oxides are present in different soil depths of the studied area.

Fraction IV (sulphides & organics) represents the sulphides and organics bound REEs in the soil. In this fraction Ce in surface soil is found in 48.15 % with maximum value indicating higher amount of sulphides and organic bound REEs. Among other REEs Nd, La, Gd, Y, Sc and Yb were found in 33.63 %, 21.54 %, 13.03 %, 13.00 %, 9.68 % and 7.87 %, respectively. In soil samples (21-40 cm) of ex-mining area sulphides and organic bound REEs become much less. Y found in highest percentage (17.66) whereas Ce and La were found in 15.16 % and 10.06 %, respectively. Other REEs were found in smaller percentages in this fraction. The same trend was found in the third layer of soil (41-60 cm). This fraction found to be more stable in nature compared to other fractions, but REEs can be mobilized and made bioavailable if suitable reducing conditions by

biodegradation of organic matter present in the ex-mining soil are provided (Haung et al., 2007, Ashraf et al., 2012).

Among all fractions of sequential extraction, most of the REEs were found in bound to silicate and residual fraction (FV). This basically accounts for the measurement of the degree of pollution. More the REEs in this fraction less will be the environmental pollution (Howari & Banat, 2001, Ashraf et al., 2012). In this fraction of soil (0-20 cm) Ce was found 32.08 % bound with silicates and residues in maximum amount, but less compared to sulphides and organics phase. Nd, La, Y, Tb, Sc, Dy and Yb were in 23.84 %, 19.50 %, 16.57 %, 10.18 %, 10.17 %, 8.15 % and 7.98 %, respectively.

The bioavailability of rare earth elements is associated with distinct physicochemical properties of soil, such as soil particulate size distribution, pH, CEC, organic matter content of the soil in this layer mostly affect the mobility of REEs. High pH leads to high REEs absorption. If such happens, it can reduce REEs mobility in the soil (Liang et al., 2014). Anthropogenic activities could be expected to change the structure of the soil. The concentration of REEs in the soil under natural conditions is mainly decided by the parent rocks, but in a mining area where soil naturally has been disturbed intensively, REEs found in higher concentrations (Hu et al., 2006). Soils with a high pH can increase the absorption of REEs due to the formation of Lanthanide complex ions (Zhu et al., 1993).

The middle layer of soil (21-40 cm) show highest amount of Ce (57 %) while Y, La, Nd, Sc, and Yb were in 16.44 %, 10.25 %, 9.32 %, 9.25 % and 7.1 %, respectively as shown in **Figure 5.3 (b)**. Other REEs found in low percentages. A major source of Ce in the soil is associated with monazite mineral used for REEs. The previous study reported in China showed the same type of analysis for REEs but in higher percentages in mining areas (Wen et al., 2001a). Radioactivity and low soluble metals (thorium and

zirconium) in complexation with REEs control their distribution in middle soil layers. Volcanic rocks, mining and refining processes and anthropogenic activities are considered a major cause of REEs in the subsoil (Mongelli et al., 2014).

The third layer of soil (41-60 cm) also show a high percentage of cerium (14.01 %) less compared to the other layers **(Figure 5.3 c).** Ce with 14.37 % constitutes much in this layer, meaning that Ce containing minerals and ores are embedded in the deeper soil. Nd found in the low amount (9.66 %) while all other REEs found in fewer amounts. Comparing the three soil layers of the studied area, it can be concluded that most of the REEs are concentrated in surface soil and their concentration decreases in the deeper soil layers. Most of the REEs found bound with adsorbed/exchanged /carbonate fractions (AEC) of the soil in the complex mineral state. Results obtained indicate REEs as harmful metals in the soil, can be transferred to other environmental components through different pathways. Speciation study of REEs can also be used to discriminate between different parental materials from ex-mining areas (Marques et al., 2012). Leaching of REEs from deep layers of soil is also possible through a sequential extraction procedure. With an increase in depth, pH also increases that caused the adsorption of REEs onto the organic matter present in the soil (Lyubomirova et al., 2011). Different pH conditions promote migration of REEs in the soils. In acidic soils, it was found 1 cm, for slightly acidic 0.5 cm and in alkaline no migration intensity was observed using isotopic tracers and numerical simulations (Zhu et al., 1996).

5.3 Potential mobility of REEs in the soil

Another advantage related to speciation is its total concentration of all geochemical fractions used for finding the potential mobility (PM) in the soils. Potential mobility is the indicator of REEs pollution in the environment. Lowering pH, CEC and organic matter content of soil increase the solubility of REEs but addition of organic acids reduce

the adsorption capacity onto the soil surface (Shan et al., 2002b). The mobility of REEs in soil is mainly influenced by REE phosphates and hydroxides (Janssen & Verweij, 2003).

A previous study on REEs (Nd, Ce, and Gd) in abandoned mine land, watershed in SWS pain report their substantial release from acid sulphate soil under acidic conditions, meaning that pH is an important factor in REEs potential mobility (Fernández-Caliani et al., 2009).

In most of the collected samples of ex-mining area, the potential mobility of REEs in the surface soil (0-20 cm) was found maximum for Y with 49.83 % and Sc with 49.54 % as shown in **Table 5.2** and **Figure 5.4 (a)**. Tb, Tm, Yb, Eu, Dy, Lu, La, Pr, Ho, Er, Nd and Gd showed 45.08 %, 41.46 %, 41.07 %, 39.96 %, 38.21 %, 36.6 %, 33.69 %, 32.97 %, 32.63 %, 27.69 %, 27.28 % and 25.19 %. A maximum concentration of Y can cause environmental hazardous risks to the surrounding soil and water quality. Y also show a distinctive character in the surface soil where it is associated with the residual fraction which ranged up to 16.57 % followed by sulphides and organic bound phase of 13 %. Although Ce content was less in AEC fraction, but silicates and residual fraction accounted higher percentage (32 %), making REEs less mobile in the soil environment. A considerable amount of Ce (48.15 %) was found in sulphides and organic bound fraction showing high stability by the formation of organic Ce bound complexes in the soil. Potential mobility of Nd in AEC fraction ranged up to 16.41 % while the residual fraction shows 13.42 %.

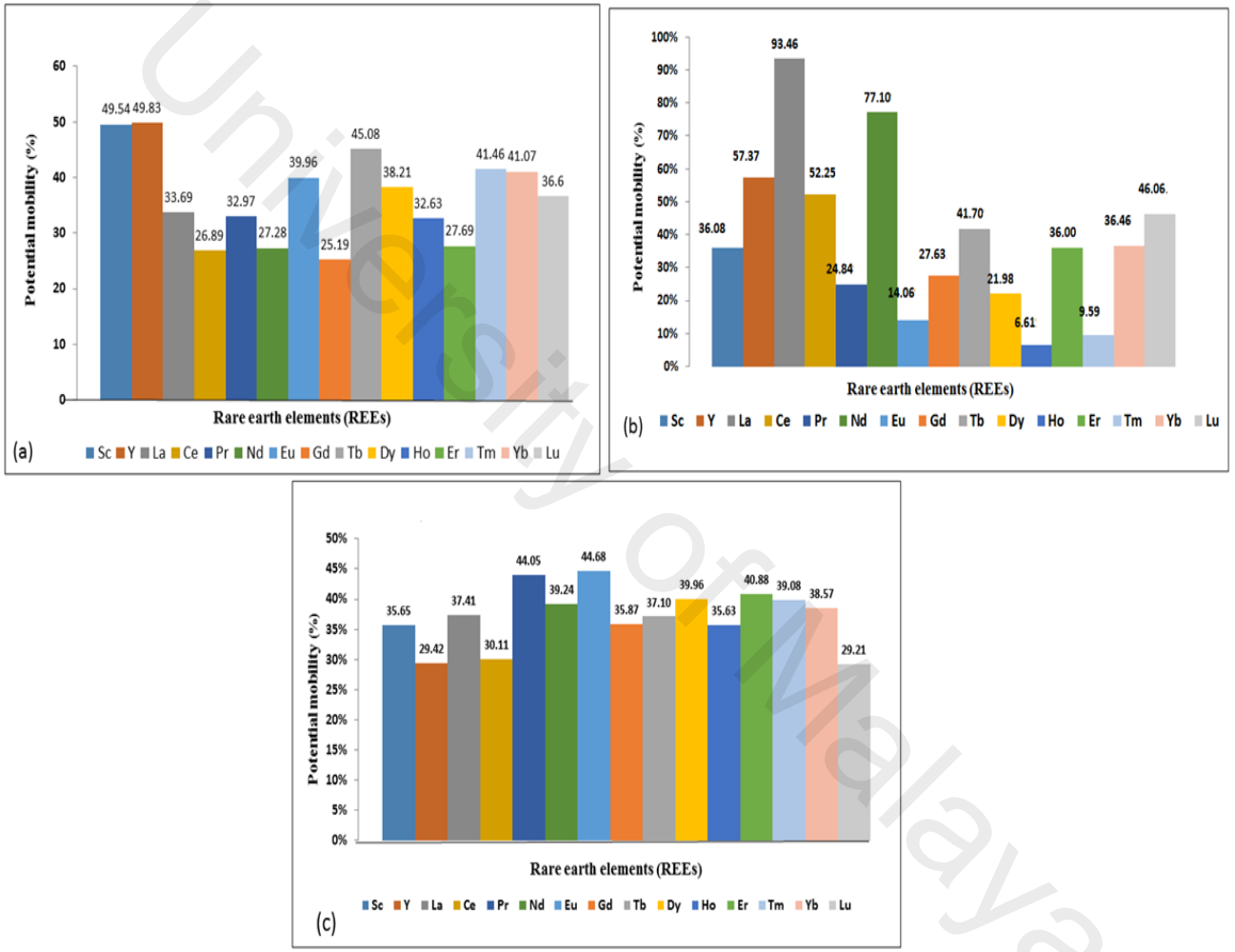


Figure 5.4: Potential mobility of soil in three different soil depths (a) potential mobility of REEs in surface soil (b) potential mobility of REEs in middle soil (c) potential mobility of REEs in deeper soil.

The highest percentage was obtained in organic bound phase (25.4 %) representing soil rich in an organic content. Amorphous and crystalline Fe oxyhydroxide bound fractions (II, III) were found in less percentage only 8.46 % and 9.35 %, respectively.

La found more in an organic bound fraction followed by residuals and AEC bound fraction. La being the chief component of monazite minerals found in the soil of remains of ex-mines in considerable amount. Under favourable conditions provided La can form complexes with a clay content of soil, oxides and metal ions forming complex ligands of greater stability. REEs in AEC bound fraction also accounts for the carbonate content of the soil ultimately facilitating their uptake by the plants, accumulating in different plant parts and disturbing the natural balance of the terrestrial environment (Islam et al., 2015). Results can suggest that under suitable conditions of pH from acidic to neutral and aerobic conditions REEs in the soil get more tendencies to form ligands and complexes in their mineral and crystalline states. Surface soil represents LREEs and HREEs having a potential to be more labile and easily available. Plants grown in such soils have more chance to take up REEs. If such situation exists, it accounts for more toxicity and bioavailability of harmful rare earth metals to the ecosystem. La and Ce were also evaluated and fractionated in road dust in Bulgaria using ICP-MS technique and indicate higher loadings on the soil surface (Lyubomirova et al., 2011).

In middle soil layer (21-40 cm) La has maximum potential mobility (93.46 %) compared to all three soil depths due to degradation of organic matter in the soil. Such high value indicates easy uptake by the plants deeply rooted into the soil system **(Table 5.2** and **Figure 5.4 b)**. Higher the potential mobility, lower will be the concentration in soil. Ce also found with 52.25 % potential mobility which is higher than surface soil. Nd also shows 77.10 % mobility which is also higher than surface soil. Potential mobility for other REEs for Ce, Lu, Tb, Yb, Sc, Er and Gd varies as 52.25 %, 46.06 %, 41.70 %,

36.46 %, 36.08 %, 36 % and 27.63 %, respectively while others have fewer percentages. The average percentage of all REEs accounts 18.86 % in AEC bound fraction, 18.30 % in organic bound and 42.73 % in silicates and residual fractions of sequential extraction.

Most of the REEs were found in the last fraction, indicating their stability and ability to form complexes with other ions present in the soil. In a study on REEs within the subsoils in Italy, research reported much higher concentrations of REEs developed from volcanic rather sedimentary materials (Mongelli et al., 2014). Amorphous Fe bound oxyhydroxides fraction contained very less REEs (7.54 %) while crystalline Fe oxyhydroxides fraction was found high in REEs with 18.63 % in all the soil samples studied from all depths representing clay-rich fraction of the soil.

Compared to other layers deeper soil layer (41-60 cm) show less REEs potential mobility with the maximum value of 44.05 % for Promethium (Pr) (**Table 5.2** and **Figure 5.4 c**). The increasing potential mobility of REEs represents the decrease in the concentration in the soil. Physical characteristics and some unknown factors of soil change the concentration and affect the potential mobility of REEs (Haung et al., 2007). It has also been demonstrated that soils having pH up to neutral and low electrical conductivity usually retained in high carbonate contents (5-10 %). In this soil layer silicates and residual fraction show maximum REEs in 15.17 %. Such distribution indicates a more compact complexation in deeper soils in the ex-mining area. Other fractions were very less in REEs. The study on speciation also indicates the higher amount of REEs in AEC fraction of sequential extraction. Adsorption, transformation into amorphous and crystalline states and co-precipitation are some of the mechanisms considered to immobilize or reduce the levels of potential mobility of REEs in the soil (Coppin et al., 2002). However, a large portion of REEs is also accounted in the residual fraction of sequential extraction. All these findings together strongly indicate that in ex-

mines of Perak, REEs are mobile and easily available. Potential mobility also points towards the bioavailability of REEs to the soil grown plants in mining areas. Higher the potential mobility higher will be the bioavailability of REEs.

Summary

This chapter describes the speciation study of REEs in sediments and soil collected from ex-mining area. Speciation has been done based on the sequential extraction procedure proposed by Tessier et al (1996). Five step sequential extraction procedure has been adopted. Novelty in this method has been developed during different steps. Based on the speciation, potential mobility has been calculated. REEs identified significantly distributed in different fractions and have considerable mobility.

CHAPTER 6: PLANT UPTAKE CAPACITY AND BIOAVAILIBILITY

6.1 Bioavailability of REEs in Plants

A number of ferns are known as accumulators of REEs. Hypogymnia physodes in mosses and lichens found good lanthanide accumulator (Dołegowska & Migaszewski, 2013). Bioaccumulation of La, Ce and Y in root surface and cortical cells was found in genera dryopteris, adiantum, dicranopteris and asplenium (Ozaki et al., 2002). Dicranopteris dichotoma show increased photosynthetic activity in the presence of REEs at acidic pH and hyperaccumulation of LREEs in chloroplast membranes and thylakoids leaves more than 0.1 % (w/w of dry mass) (Wang et al., 2003). Appropriate mechanism for REEs reduction to divalent state has not fully clarified (Zhang et al., 2013). Cerium (Ce) with the oxidation state of +3 in horseradish was found to migrate in plant body but also found in tropical tree barks (Guo et al., 2007). In vascular plants, REEs found much concentrated in roots than in leaves and stems with the lowest amount in fruits and seeds (Xu et al., 2003). It was found that ferns and lichens accumulate higher amounts of Y as compared to other genera (Maksimovic et al., 2014, Ozaki et al., 2002).

In this study REEs concentration in plants was identified and the role of different soil properties on the solubility and bioavailability in the plant. From these observations, possible transfer of REEs into the plants and their bioaccumulation was also evaluated

6.1.1 Soil analysis

The physical parameters and REEs concentration in soils in different sampling sites are listed (**Table 4.12** and **Table 4.13**). The accuracy of the REEs analysis was confirmed by determination of rare earth elements in a standard reference material (2586) (**Table 3.3**).

The highest concentration of cerium (Ce) (420.5 mg kg^{-1}) was detected at P1. Soils of two plant samples (P2 and P8) contain Ce 256.49 and 269.82 mg kg^{-1} respectively. Neodymium (Nd) was found in maximum concentration at P2 (112.3 mg kg^{-1}) while other soils (P3, P6, P7 and P8) contain 88.64, 85.05, 75.35 and 82.11 mg kg^{-1} respectively. Soils from sampling site P3, P5, P6 and P8 were enriched with La concentration of 94.69, 62.11, 65.37, 59.69 and 60.16 mg kg^{-1} respectively. La and Ce at low concentration may not cause any problem, but at higher concentration cause significant damage to the ecosystem (Barry and Meehan, 2000). Yttrium was found in considerable amount only at two plant sample (P1 and P5) with 79.2 and 84.7 mg kg^{-1} respectively. Scandium (Sc) was found at P5 and P8 soils with concentration of 51.47 and 47.17 mg kg^{-1} respectively.

6.1.2 Uptake capacity and bioavailability of REEs

The plants collected for REEs are summarized in **Table 6.1 and Figure 6.1**. Plant species (P9, P10 & P11) are abundantly found in ex-mining area and are discussed in section 6.2 whereas P12 and P13 are described in section 6.3.

Table 6.1: Plant species with the family names, plant codes, habitat and uptake behaviour.

Family	Specie	Plant code	Habitat	Uptake capacity
Gleicheniaceae	*Dicranopteris dichotoma.*	P1	Mining area	hyperaccumulator
Gleicheniaceae	*Dicranopteris linearis(Burn) (A)*	P2	Mining area	accumulator
Gleicheniaceae	*Dicranopteris linearis(Burn) (B)*	P3	Natural area	hyperaccumulator
Melastomataceae	*Melastoma malabathricum L.*	P4	Industrial area	hypertolerant
Cyperaceae	*Cyperus difformis Rottb.*	P5	Road side	tolerant
Cyperaceae	*Cyperus kyllingia Rottb.*	P6	Road side	accumulator
Cyperaceae	*Cyperus distans L.*	P7	River side	accumulator
Cyperaceae	*Cyperus rotundus L.*	P8	River side	hyperaccumulator
Laminaceae	*Hyptis suaveolens L.*	P9	Natural area	tolerant
Fabaceae	*Albizia Myriophillia*	P10	Mining area	hyperaccumulator
Poaceae	*Eleusine indica L.*	P11	River side	hyperaccumulator
Euphorbiaceae	*Ricinus communis L.*	P12	Mining area	hyperaccumulator
Astraceae	*Emilia sonchifolia*	P13	Residential area	hyperaccumulator

Main root of plants, especially (*Dicranopteris dichotoma (P1), Dicranopteris linearis (A) (P2) and Cyperus rotundus L. (P8)* show a very high concentration of REEs as compared to stem. *Dicranopteris linearis (B) (P3), Melastoma malabathricum L (P4), Cyperus difformis Rottb (P5), Cyperus kyllingia Rottb (P6) and Cyperus distans L.(P7)* are among the plants that showed the highest concentration of REEs in leaves. REEs are not considered as essential to the plants, but however plants can absorb REEs from the soil through the roots and also through leaves from the atmosphere polluted with REEs mainly from mining areas. Common plants under natural condition have low REEs concentration around 10^{-3}- 10^{-1} µg g^{-1} dry mass (Wang et al. 1997). In mining areas of China high levels of REEs have been found (Liang et al., 2014). Different plant species express different variations of REEs concentration are given in **Table 6.2**.

Lanthanum concentration ranged up to 568.90 and 413.80 µg g^{-1} in *Cyperus rotundus L* (P8) and *Cyperus distans L.* (P7) plant species respectively. Sc concentration was found about 759.60 µg g^{-1} in *Cyperus distans L* (P7) species and 220.93 µg g^{-1} in *Cyperus rotundus L (*P8) plant species. Yttrium (Y) was obtained in lower concentration 204.60 µg g^{-1} in *Cyperus rotundus L.* (P8) while 640.43 µg g^{-1} in *Cyperus distans L.* (P7).

The results indicate different concentration levels of REEs in different plant species. Here we focus more on LREEs as shown in **Figure 6.2**. All species of cyperaceae show REEs in variable amounts. *Cyperus rotundus L (P8)* found hyperaccumulator for REEs. *Cyperus distans L. (P7)* investigated and set up as the accumulator. *Cyperus difformis Rottb.(P5)* regarded as tolerant while *Cyperus kyllingia Rottb.(P6)* acts as the accumulator to REEs uptake from soil.

Figure 6.1: Plant species analyzed for REEs from ex-mining area.

Continued

Figure 6.2: Plant species analyzed for REEs from ex-mining area. (Continued)

Table 6.2: Plant species with individual REEs (µg g^{-1}) in different plant parts and their LREEs and HREEs capacity.

	Dicranopteris dichotoma. (P1)			*Dicranopteris linearis (A) (P2)*				*Dicranopteris linearis (B)(P3)*				*Melastoma malabathricum L.(P4)*		
	(leaves)	(shoot)	(Root)	(Root)	(shoot)	(Petiole)	(Lamina)	(Root)	(shoot)	(Petiole)	(Lamina)	(shoot)	(Root)	(Leaves)
Sc	33.16	33.40	177.83	574.43	66.53	35.47	366.50	312.41	24.53	26.57	478.50	9.50	12.47	126.53
Y	219.07	57.70	111.65	289.67	45.41	12.38	339.47	452.57	11.62	4.48	1009.63	9.91	14.53	84.61
La	1568.00	59.39	1305.07	465.37	101.32	41.50	355.67	585.40	48.27	21.52	401.47	28.40	36.43	158.59
Ce	2290.33	738.63	1482.60	350.60	95.50	18.50	406.70	725.57	98.66	13.45	706.57	48.52	118.53	187.44
Pr	149.77	48.53	566.70	58.54	25.79	19.37	115.50	42.56	5.60	3.53	362.30	10.48	15.20	41.56
Nd	1499.00	112.23	687.40	150.40	16.44	10.59	198.50	54.58	6.45	4.26	286.50	20.30	33.55	49.13
Eu	29.32	12.53	161.55	16.64	3.65	8.29	18.48	15.46	3.22	3.19	24.12	6.44	7.52	10.49
Gd	75.08	47.49	157.63	19.56	6.60	9.99	79.47	96.64	3.23	15.58	204.50	14.31	25.66	139.52
LREEs	732.97	138.74	581.30	240.65	45.16	19.51	235.04	285.65	25.20	11.57	434.20	18.48	32.99	99.73
Tb	85.37	45.85	98.40	7.50	3.58	4.47	7.77	41.51	7.80	4.13	257.50	6.62	7.29	77.30
Dy	47.78	17.11	166.30	22.47	10.86	2.85	59.50	68.57	3.29	2.87	122.43	16.47	22.36	81.33
Ho	13.24	6.39	59.39	5.66	1.26	2.59	5.62	2.23	1.89	1.67	2.45	4.50	7.83	15.57
Er	13.24	6.56	34.58	12.45	4.58	1.30	8.56	16.42	3.73	1.45	26.77	6.55	9.75	12.31
Tm	8.37	13.50	17.57	4.96	4.55	1.52	2.67	2.50	1.26	0.43	35.73	4.55	5.45	21.43
Yb	18.49	15.45	151.56	13.50	8.64	2.43	91.50	58.44	3.23	1.45	143.63	11.55	34.66	66.43
Lu	7.48	6.18	16.10	3.26	1.18	1.28	5.81	1.87	0.97	7.85	19.50	6.60	7.33	13.56
HREEs	27.71	15.86	77.70	9.97	4.95	2.35	25.92	27.36	3.17	2.84	86.86	8.12	13.53	41.13
TF		4.00				5.34				3.20			10.30	
BCF		53.74				97.19				151.11			64.26	
BAF		143.39				219.16				230.87			103.91	

Continued

	Cyperus difformis Rottb.(P5)			*Cyperus kyllingia Rottb.(P6)* *Cyperus distans L.(P7)*							*Cyperus rotundus L.(P8)*			
	(Root)	(Leaves)	(Flower)	(Root)	(Leaves)	(Flower)	(Stem)	(Root)	(Leaves)	(Flower)	(Root)	(Stem)	(Leaves)	(Flower)
Sc	62.61	221.37	10.90	17.58	58.87	6.84	30.50	175.63	640.43	15.48	280.83	18.84	204.60	8.21
Y	8.84	10.43	5.79	11.75	37.57	6.46	49.60	148.33	759.60	7.47	316.33	125.73	220.93	11.58
La	29.70	17.71	6.87	10.44	365.84	6.45	145.63	206.60	413.80	32.67	933.60	396.40	568.90	27.70
Ce	59.72	24.96	7.72	16.35	410.63	25.17	123.60	213.97	684.47	47.53	1347.53	339.69	2283.67	18.09
Pr	8.44	16.25	4.10	6.37	5.44	6.78	82.36	38.30	85.27	7.78	450.67	52.43	153.40	8.34
Nd	15.56	13.65	5.72	9.36	315.81	7.40	82.47	140.17	231.53	8.45	222.60	115.33	503.70	10.62
Eu	6.03	6.47	5.61	6.48	6.45	6.47	21.37	8.70	71.62	5.29	27.14	6.77	9.65	3.12
Gd	11.83	36.53	9.46	6.52	87.30	5.16	74.41	32.43	58.47	10.59	227.53	118.20	175.80	8.68
LREEs	25.34	43.42	7.02	10.61	160.99	8.84	76.24	120.52	368.15	16.91	475.78	146.67	515.08	12.04
Tb	5.86	12.53	4.88	4.64	244.47	2.39	155.13	6.78	9.52	6.74	289.50	77.45	35.14	5.84
Dy	7.26	13.12	5.53	6.46	125.60	6.53	21.25	61.47	52.57	4.60	217.92	31.53	188.60	9.80
Ho	5.37	12.26	4.40	5.06	15.09	4.46	3.50	16.63	11.57	1.65	16.42	6.33	33.36	7.26
Er	6.61	5.64	5.11	6.02	35.55	3.77	10.20	8.43	15.43	5.31	18.47	4.51	34.64	7.60
Tm	6.38	3.65	1.59	6.95	62.76	1.30	3.30	7.43	14.59	2.25	6.14	3.54	18.38	2.26
Yb	4.74	5.70	3.83	7.77	134.72	2.19	17.76	129.59	17.24	2.00	412.73	114.68	210.68	2.60
Lu	4.87	6.21	6.05	3.82	15.27	6.05	2.62	10.41	7.75	6.05	3.59	1.63	27.52	8.59
HREEs	5.87	8.44	4.48	5.82	90.50	3.81	30.54	34.39	18.38	4.09	137.82	34.24	78.33	6.28
TF		7.26			3.60			34.76				4.90		
BCF		12.39			99.94			151.70				134.13		
BAF		23.49			118.97			299.87				387.11		

*REEs individual values in different plant parts measured in μg g-1

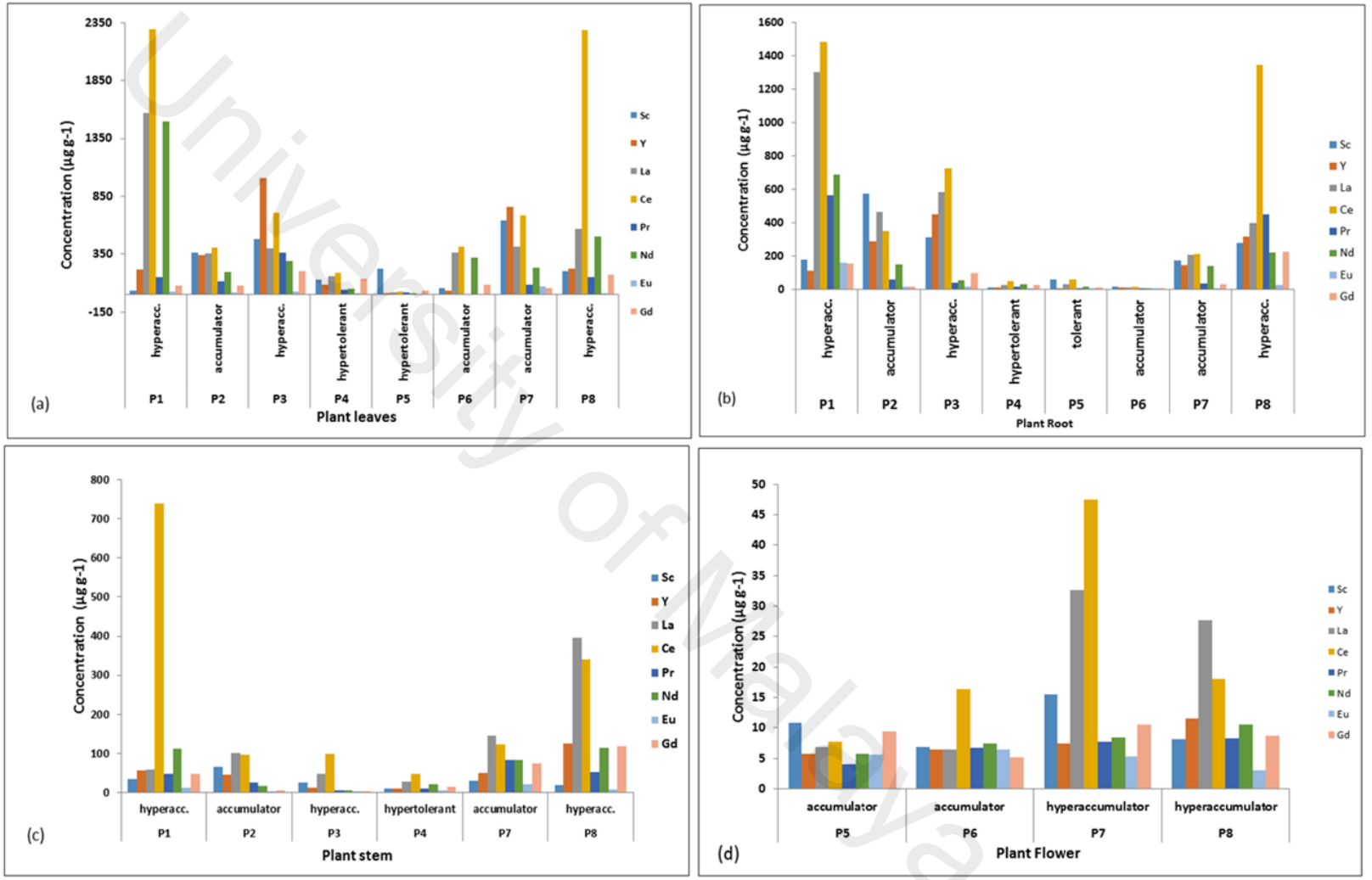


Figure 6.3: (a) REEs distribution in the leaves of plant species (b) accumulation of REEs in the root parts (c) REEs in plant species having stem (d) REEs in flowering plants. P1= *Dicranopteris dichotoma.*, P2, P3 = *Dicranopteris linearis(Burn) (A)(B)*, P4= *Melastoma malabathricum L*, P5= *Cyperus difformis Rottb*, P6= *Cyperus kyllingia Rottb.*, P7= *Cyperus distans L.*, P8= *Cyperus rotundus L.*].

Maximum uptake capacity in roots among the plants from cyperaceae were found in *Cyperus rotundus L.(P8)* which present highest concentration of Ce, La, Sc, Y, Pr, Nd, Eu and Gd in their roots about 1347.53, 396.40, 280.83, 316.33, 556.7, 687.4, 161.55, 157.63 µg g^{-1} respectively. Leaves of the *Cyperus rotundus L.(P8)* show highest Ce concentration up to 2283.67 µg g^{-1} while *Cyperus distans L. (P7)* indicate 684.47 µg g^{-1} in their leaves.

Of the four Cyprus species only two species, having stem in them were analyzed for REEs. Shoot of *Cyperus rotundus L.(P8)* shows Sc, Y, La, Ce, Pr, Nd, Eu and Gd concentrations 18.84, 125.73, 396.4, 339.69, 52.43, 115.33, 6.77, 118.20 µg g^{-1} respectively, while shoot of *Cyperus distans L.(P7)* found abundant in Sc, Y, La, Ce, Pr, Nd, Eu, and Gd concentrations 30.50, 49.60, 145.63, 123.60, 82.36, 82.47, 21.37, 74.41 µg g^{-1} respectively. Flowers from four plants [*Cyperus difformis Rottb (P5)*; *Cyperus kyllingia Rottb (P6)*; (*Cyperus distans L (P7*); *Cyperus rotundus L* (*P8*)] also investigated for REEs **(Table 6.2** and **Figure 6.2).** Flowers from *Cyperus distans L (P7)* found rich in Sc, Ce, La, Pr, Eu, Nd, and Gd while P8 were yttrium rich. Plant species *Cyperus difformis Rottb (P5)*; *Cyperus kyllingia Rottb (P6)* show considerable concentration levels of these REEs in their flowers.

Three species of ferns belonging to family *Gleicheniaceae* were also evaluated for their uptake capacity for REEs from mining soil. *Dicranopteris dichotoma (P1), dicranopteris linearis (Burn) (A) (P2)* and *dicranopteris linearis (Burn) (B) (P3)* were sampled from different location in an ex-mining area. *Dicranopteris linearis (Burn) (A, B)* samples from two different locations were divided into four parts (root, shoot, petiole and lamina) and analyzed for REEs. The levels of all REEs in fern species is given in **Table 6.2** while uptake capacity for LREEs (Sc, Y, La, Ce) is indicated in **Figure 6.2**.

Roots of *dicranopteris dichotoma (P1)* have the highest concentration of Ce and La with 1482.60 and 1305.07 µg g^{-1} while Sc and Y were low in concentration with 177.83 and 111.65 µg g^{-1} respectively. Such high level of La can damage the plant growth and disturb the plant physiology (von Tucher & Schmidhalter, 2005). Leaves (petiole and lamina) also show hyper accumulation of Ce and La with 2290.33 and 1568 µg g^{-1} with small amounts of Sc and Y. The shoot of *dicranopteris dichotoma (P1)* shows the maximum level of Ce 738.63 µg g^{-1} among all fern species. This indicates that most of the REEs are accumulated by this plant and can be transferred to other parts easily (Shan et al., 2003). Such results from the ex-mining area compared to another mining area in china are less in assessing the bioavailability levels of REEs in ferns where REEs varied 926.43 in root, 137.63 in stem, 136.66 in petiole and 2648.97 µg g^{-1} in the lamina (Liang et al., 2014).

Dicranopteris linearis (Burn)(B) roots found Ce 725.57 µg g^{-1} while *dicranopteris linearis (Burn)(A)* possess less Ce 350.60 µg g^{-1} in its roots compared to other two species. La, Sc and Y in both species of *Dicranopteris linearis (Burn) (A, B)* found in approximately same amounts as shown in Table 4. La, Ce, Sc, and Y found higher in the leaves of *dicranopteris linearis (Burn)(B)* with 401.47, 706.57, 478.50 and 1009.63 µg g^{-1} respectively than *dicranopteris linearis (Burn)(A).* Shoot of *dicranopteris linearis (Burn)(B)* possesses more Ce levels 98.66 µg g^{-1} compared to *dicranopteris linearis (Burn)(A)* whose stem found rich in La, Sc and Y with 101.32, 66.53, 45.41 µg g^{-1} respectively. It can be concluded that the stem of fern species has more tendency to uptake REEs from the roots and transfer to the leaves. When the concentration of REEs become lower in the surroundings, *dicranopteris linearis (Burn)(A)(B)* show more tendency to uptake but it becomes less when REEs are largely present around the plant grown soil. The study also concludes that most of the LREEs in the ferns come from soil from the ex-mining area.

Another plant species analyzed for REEs was *Melastoma malabathricum L. (P4)* from family *Melastomataceae* as shown in **Figure 6.2** and **Table 6.2**. This plant recognized as hyper tolerant for REE uptake from the soil. The plant is divided into roots, shoot, and leaves. Very small concentrations have been found in different parts of this plant. Cerium found the maximum in 48.52 µg g^{-1} concentration in roots and shoot while leaves have the variable concentration of Sc, Y, La and Ce with values 126.53, 84.61, 158.59, 187.44 µg g^{-1} respectively. Such indicate the transformation and deposition levels of REEs from roots to leaves or from atmospheric particulate matters. Among all plant species distribution of REEs follow the order: leaves > roots> shoot > flower. The concentrations of individual REEs in all plants belonging to different families are not of the same sequence. But the distribution patterns of REEs roots are quite similar to the REEs in their soils (Zhenggui et al., 2001).

6.1.3 Distribution of LREEs and HREEs among different plant parts

The concentration of light rare earth elements (LREEs) in the adventitious roots, stem, leaves and some petiole and laminas of the plants were determined are shown in **Figure 6.3.** LREEs were mostly found in roots and leaves (petiole, lamina) of the studied plants. Almost all plants (except P4) found enriched with LREEs having mean concentration 207.23 µg g^{-1}. The maximum value of LREEs was 732.97 and ranged from 7.02 – 723.2 µg g^{-1}. *Dicranopteris dichotoma (P1)* and *Dicranopteris linearis (B)* were nominated as LREEs hyperaccumulators. The sum of LREEs in different parts of ferns and P4 plant are root> lamina > stem > petiole. This indicates that due to higher translocation function of stem and petiole, less LREEs found accumulated in them. At some sampling locations, concentration of LREEs also varies as lamina > root > stem > petiole.

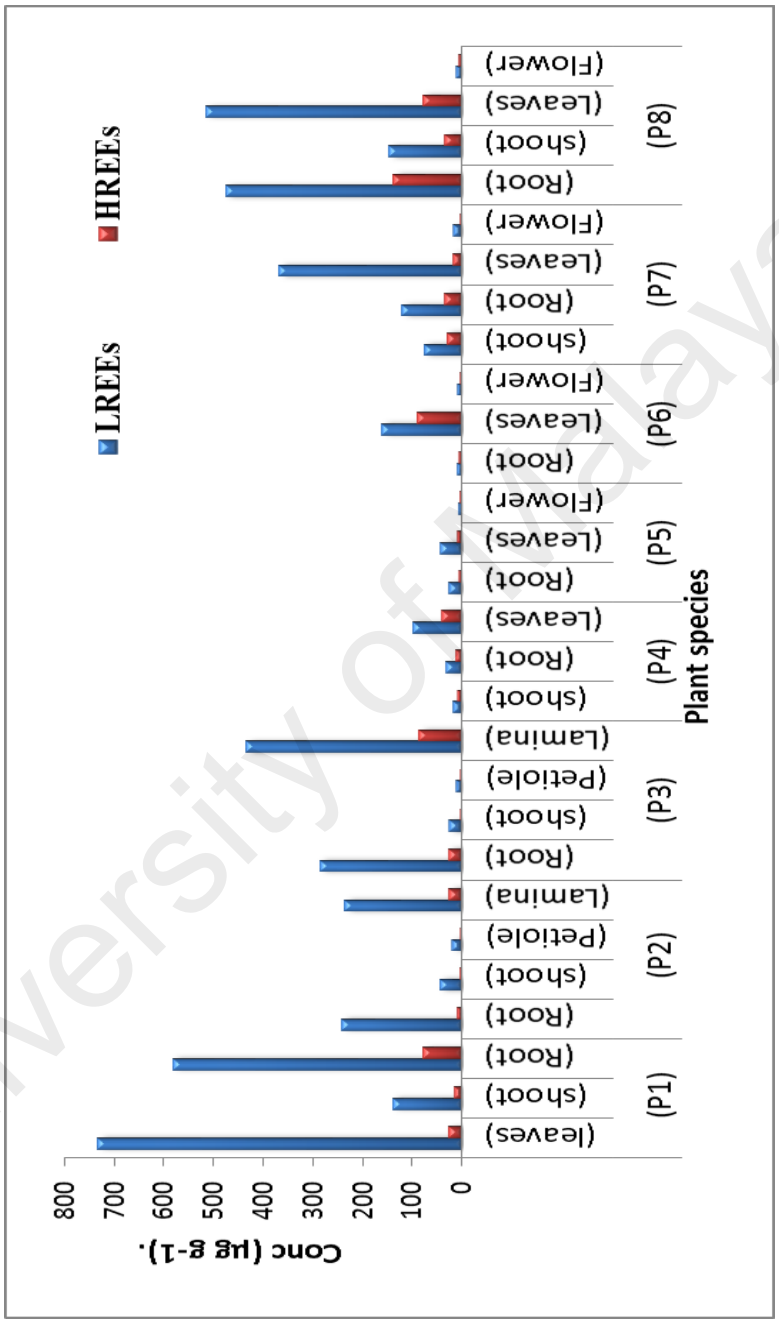


Figure 6.4: Accumulation of LREEs and HREEs in different parts of plants in study area.

Average values for LREEs among ferns species varied as 141.97 µg g^{-1} in all parts of plants with the maximum value of 515.8 and ranged FROM 7.02 - 508.06 µg g^{-1}. This result is consistent with the study with Zhenggui et al. (2001) who determined REEs in order of lamina > root > stem > petiole. Most of the Cyprus species (P5, P6, P7, P8) accumulate LREEs. Low pH increased the release of LREE from the soil and uptake by the plant roots (Shan et al., 2003). Presence of large amounts of LREEs in the leaves involved mechanism for LREEs hyper accumulation. Order of uptake of LREEs by different plant species studied described as follows: P1 > P8> P3> P7> P2> P6> P4> P5.

The abundance of HREEs in shoot, leaves, lamina and petiole of the plants studied from the ex-mining area found lower than those in the roots. Average HREEs values were found 33.07 with highest value 137.82 and ranged from 2.35 - 134.04 µg g^{-1}. Order of uptake of HREEs from the soil by the plants was found as P8> P6> P3> P1> P5> P4> P7> P2.

6.1.4 Translocation, Bioconcentration and Bioaccumulation of REEs

Over the last decades, translocation, bioaccumulation and bioconcentration of REEs in various environmental samples have been widely discussed (Ndeda & Manohar, 2014, Liang et al., 2014). Evaluation of REEs toxicity, especially in ex-mining areas has become increasingly important due to the harmful impacts on human. Many countries including China have evaluated their mining area for soil-plant system and found significantly high levels of REEs in plants through various transport processes compared to natural areas. Most of the REEs under normal conditions found deposited on the solid surface such as upper soil layer (Jones, 1997). In this study soil analysis also confirmed that most of the REEs are indicated in the soil. REEs usually changed under different environmental conditions but mining and ex-mining area still found overloaded with REEs (Xing-kai, 2005). REEs from soil are taken up by plants and transferred to all other

parts. Generally, 80% of the REEs found concentrated in the roots. Many researchers work on the uptake of REEs by plants in cultured nutrients, their results follow the order: root > stem > leaf >flower > fruit (Tagami and Uchida, 2006). However, REEs mining area grown plants show different results in hyperaccumulation plants (Zhang et al., 2001b, Fu et al., 2001b).

6.1.4.1 Translocation factor (TF)

Maximum TF values from P1- P8 plants species are 0.77 (Tm), 0.92 (Tm), 0.85 (Ho), 0.90 (Lu), 0.97 (Lu), 1.25 (Pr), 22.8 (Tb) and 0.58 (Tm) respectively as shown in **Figure 6.4**. TF was found highest in plant sample P7. The sum of the translocation factor (TF) ranged from 3.2 to 34.76 for all the plant species (P1-P8).

6.1.4.2 Bioconcentration Factor (BCF)

Bioconcentration factor for all REEs **(Figure 6.4)** indicate variations in different plants. Maximum BCF value for all studied plants from P1 to P8 found 16.6 (La), 18.5 (Sc), 35.3 (Y), 10.2 (Ho), 1.6 (Ho), 20.3 (Tb), 32.8 (Eu) and 29.4 (Yb) respectively. Values > 1 represent bioconcentration of REEs in the plant species from the ex-mining area. From **Figure 6.4,** it is concluded that BCF is higher for plants P1, P2, P3, P6, P7, and P8. The sum of the BCF for plant species varies as for P1 (53.74), P2 (97.19), P3 (151.11), P4 (64.26), P5 (12.39), P6 (99.94) P7 (151.7) and P8 (134.1) indicating accumulator and hyperaccumulator behavior of REEs. Plants having BCF values greater than 1 can be used for REEs removal from the soil. Previous studies from mining areas of China indicate accumulation of LREEs up to 7,000 μg g^{-1} *in Dicropteris dichotoma* dry leaf biomass (Shan et al., 2003).

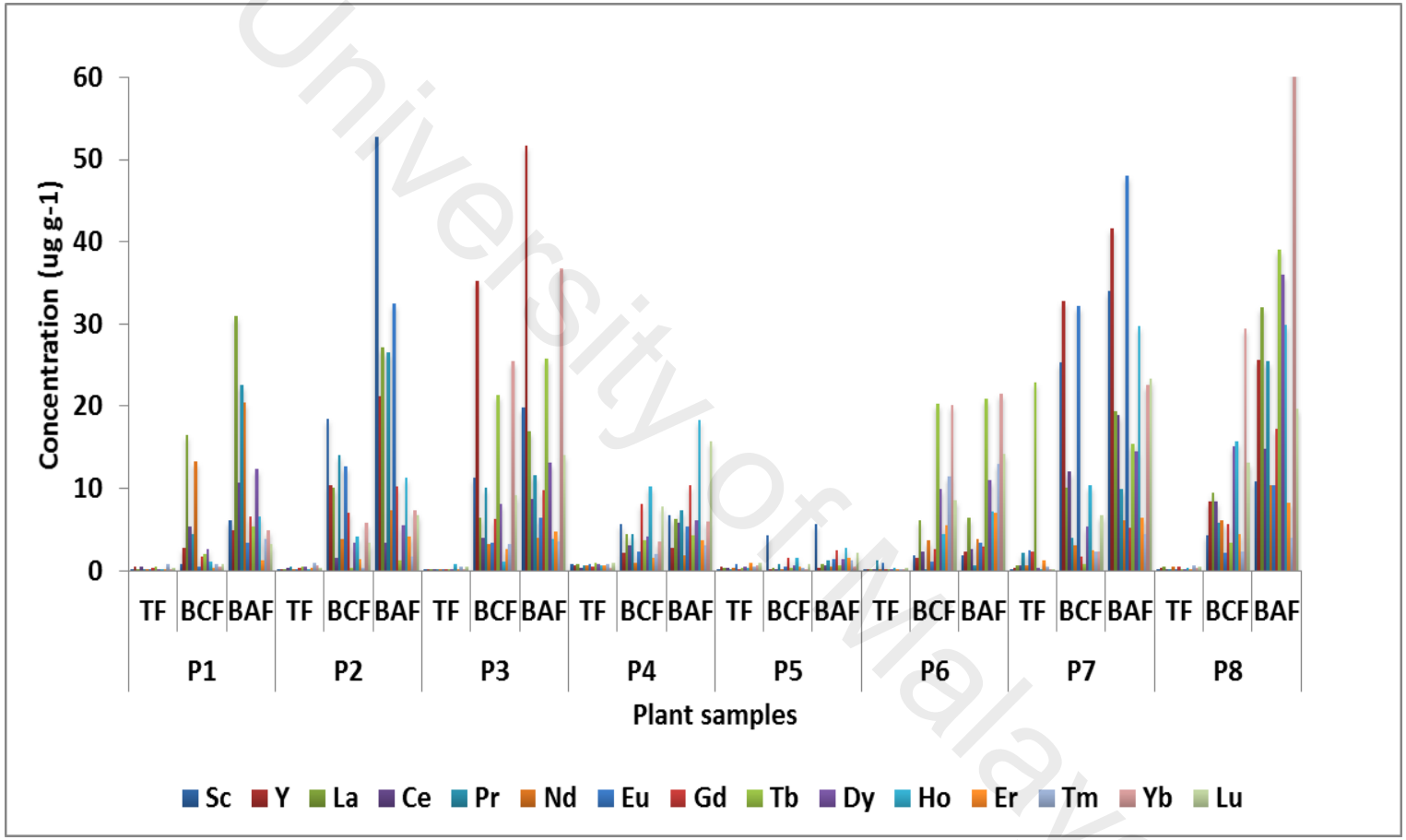


Figure 6.5: Rare earth elements (REEs) contents in all parts of the plants with their translocation factor (TF), bioconcentration factor (BCF) and bioaccumulation factor (BAF).

The plant species with higher BCF together with soil alteration enhance the plant availability of REEs in soil fractions hold promise for phytoextraction and consequently an in situ bioremediation of the dump field.

6.1.4.3 Bioaccumulation Factor (BAF)

BAF values in plant species analyzed for REEs were range from 5.7 to 103.3 **(Figure 6.4).** Different plants accumulate different REEs in different concentrations. BAF value for each plant was found as; P1 31(La), P2 52.8 (Sc), P3 51.6 (Y), P4 18.4 (Ho), P5 5.7 (Sc), P6 21.6 7(Yb), P7 48 (Eu) and P8 103.3 (Yb). The results indicate that such BAF values are good in phytoextraction of REEs from the soils. Plants belonging to different families have the ability to uptake REEs from the soil and bioaccumulate. Uptake capacity of REEs usually follows the route from roots to shoot and shoot to leaves and finally from leaves to fruit. It is considered that all REEs are reduced to the divalent state during migration in plant body (Tian et al., 2003). The sum of the BAF for plant species varies as for P1 (143.39), P2 (219.16), P3 (230.87), P4 (103.91), P5 (23.49), P6 (118.97) P7 (299.87) and P8 (387.11) indicating hyperaccumulation of REEs.

Consistent with current findings, roots have the higher REEs concentration in plant species analyzed from the ex-mining area. The trends were quite similar to the previous work on the uptake of REEs in plants grown in the soils of mining areas and varying chemistry (Thomas et al., 2014, Zhenggui et al., 2001). Accumulation of REEs in the shoot and leaves lead to the most toxic effects on plants as this region considered of primary importance in photosynthesis.

6.2 Uptake capacity and bioavailability of REEs in abundantly wild plants

6.2.1 Plant species and their uptake capacities

Hyptis suaveolens L. is another fast growing herb belonging to family Lamiaceae, also found in tropics. This herb originated from tropical America, but now considered as

worldwide weed (Chukwujekwu et al., 2005, Vera-Arzave et al., 2012). *Albizia myriophillia* belong to the family Fabaceae and is abundant in most of the tropical and subtropical regions of the world. Commonly it is known as "Cha-em Thai" because of extensive use of this herb in traditional medicines (Joycharat et al., 2013). *Eleusine indica L* is an annual grass belongs to a family Poaceae and is also known for its medicinal properties (Malan and Neuba, 2011). Overall plant species with their habitats and uptake capacities are shown in **Table 6.1** and plants are represented in **Figure 6.1.**

Many metals have been previously found in medicinal plants (Hussain et al., 2011). Lahat ex-mining areas also have diversity of these plants grown onto the soil. Due to REEs abundance in nature as emerging pollutants, there is a need to ensure the presence and levels of concentration of REEs into the plants.

6.2.2 Distribution of REEs in soil from ex-tin mining areas

Good agreement between the analyzed and certified values was obtained for analyzed REEs. To assess linear adjustment of a data to linear model value ~ equal to 1 indicate good accuracy. In the calibration plot, the correlation coefficient (r^2) obtained was from 0.996 to 0.998, depending on the element. The accuracy and analytical precision of the measurements are reported as the percentage recovery (%), limit of detection (LOD), limit of quantification (LOQ) and CV % in **Table 3.4** as described earlier in chapter 3. The recoveries of REEs being analyzed were from 90 - 97 % for apple leaves (de Oliveira et al., 2016) and 82.3 – 100 % for spinach leaves. Quality control and element concentrations in this study were found satisfactory.

Physical parameters and the concentration of all REEs in the soils collected from different plant locations are reported in **Table 6.3.** pH of the soil ranged from 4.4 - 7.5. Electrical conductivity varied from 9.18-112.2 µs cm^{-1}. Cation exchange capacity (CEC) was found from 9-32 cmol kg^{-1}. Organic matter content was in the range 5-21 %,

indicating less organic matter in the soil. Soil textural analysis showed soil rich of sand (~86 %). Lower pH values, CEC, and organic matter content increase the solubility of REEs in the soil (Cao et al., 2001, Khan et al., 2016). The average concentration of REEs in soil samples was 46 mg kg^{-1}.

In this study cerium (Ce) was detected at P1 in high concentration 420.5 mg kg^{-1}. Soils of the plant sample (P2) contain Ce 256.49 mg kg^{-1}. Neodymium (Nd) was found in maximum concentration at P10 (112.3 mg kg^{-1}) while P11 soil contain 88.64 mg kg^{-1}. Soils from sampling site P11 was found enriched with La concentration 94.69 mg kg^{-1}. Lanthanum and cerium at low concentration may not cause any problem, but at higher concentration cause significant damage to the ecosystem (Barry & Meehan, 2000). Yttrium was found in considerable amount only at P9 with 79.2 mg kg^{-1}. Europium (Eu) concentration was maximum at P9 (59.84 mg kg^{-1}). Gadolinium (Gd) and terbium (Tb) were same in soil P9 (42.26 mg kg^{-1}) while other REEs were below 40 mg kg^{-1}.

Table 6.3: Physical characteristics of the soil from ex-mining land and its distribution of REEs.

Parameters	***Hyptis suaveolens L.*(P9)**	***Albizia myriophillia* (P10)**	***Eleusine indica L.*(P11)**
pH	4.4 ± 0.02	6.1 ± 0.05	6.4 ± 0.01
EC (µs/cm)	27.18 ± 0.11	9.72 ± 0.08	95.41 ± 0.24
CEC(cmol/kg)	30 ± 0.42	23 ± 0.19	11± 0.11
OM (%)	19 ± 0.16	19 ± 0.11	10 ± 0.08
Sc	39.89 ± 0.38	19.77 ± 0.24	42.52 ± 0.19
Y	79.2 ± 0.17	32.44 ± 0.11	28.63 ± 0.11
La	94.69 ± 0.33	35.48 ± 0.01	62.11 ± 0.22
Ce	420.5 ± 0.05	256.49 ± 0.17	176.16 ± 0.16
Pr	33.79 ± 0.25	8.24 ± 0.32	35.86 ± 0.11
Nd	112.3 ± 0.45	50.95 ± 0.22	88.64 ± 0.32
Eu	59.84 ± 0.17	1.45 ± 0.62	7.11 ± 0.44
Gd	42.26 ± 0.08	11.35 ± 0.03	32.65 ± 0.11
Tb	42.26 ± 0.43	18.74 ± 0.18	12.03 ± 0.26
Dy	18.66 ± 0.09	17.19 ± 0.15	15.08 ± 0.17
Ho	12.12 ± 0.12	1.34 ± 0.24	2.18 ± 0.05
Er	43.5 ± 0.01	6.41 ± 0.01	10.22 ± 0.12
Tm	10.15 ± 0.55	8.18 ± 0.24	11.06 ± 0.36
Yb	38.23 ± 0.18	15.75 ± 0.22	5.63 ± 0.19
Lu	9.33 ± 0.35	1.72 ± 0.15	2.14 0.25

6.2.3 Determination of REEs in wild plant species (*Hyptis suaveolens L., Albizia myriophillia and Eleusine indica L.)*

Development in industrialization such as mining, refining, smelting, along with the use of fertilizers and pesticides has caused the pollution of the environment. Soil is being much polluted environmental component by these heavy and rare earth metals (REEs). Previous studies show uptake of rare metals from mining area in considerable concentrations but little data is available for REEs (Dingjian, 2012, Liang et al., 2014, Tagami & Uchida, 2006). In turn plants are getting deposited by REEs and finally reaching the food chain (Kulhari et al., 2013). In this study significant differences in the uptake of REEs by analyzing parts (root, stem, leaves and flower) of all the medicinal plants were observed. Results explain the accuracy of data via SRM recovery, ranging from 95-102 % for apple leaves (1515a) (de Oliveira et al., 2016) and 83-110 % of spinach leaves (1570a) given in Table 3.4. The results of the analysis for REEs in the root, stem, leaves and flower of these plants are summarized in **Figure 6.5** and **Table 6.4.**

Root is the major organ of a plant that has the capacity to uptake REEs from the soil and transfer to other parts of the plant (Tagami & Uchida, 2006, Zhang et al., 2002). Root of *Hyptis suaveolens L* absorb 17.9 μg g^{-1} Ce, 12.65 μg g^{-1} Sc, 17.47 μg g^{-1} Nd, 16.21 μg g^{-1} La, 11.12 μg g^{-1} Y, 10.81 μg g^{-1} Gd, 6.93 μg g^{-1} Eu, 9.67 μg g^{-1} Pr, 9.2 μg g^{-1} Tb, 7.21 μg g^{-1} Dy and 9.56 μg g^{-1} Yb given in **Figure 6.5 (a).** Other REEs were found in low concentrations. Ce and Nd were in higher concentration in the root of *Hyptis suaveolens L*. The stem of the *Hyptis suaveolens L* **(Fig 6.5 a)** contains small concentrations of REEs having 4.12 μg g^{-1} for Gd and 3.17 μg g^{-1} La. Leaves contain the maximum amount of a Eu (7.98 μg g^{-1}) and Ce (7.16 μg g^{-1}). Previous study reported by Mishra and Tripathi (2009) also indicate the higher metal accumulation by *Hyptis suaveolens* (Mishra & Tripathi, 2009).

By comparing the root, stem and leaves of *Hyptis suaveolens L* maximum amount of Ce (17.9 μg g^{-1}) was found in the roots. This study concludes that most of the LREEs are taken up by the roots of the plants and transfer to other parts of the plant. Some REEs found to enhance the growth of the plants, but if these metals deposits in large amount then negative impacts can also be seen (von Tucher & Schmidhalter, 2005).

Sc, La, Nd and Ce are the major components of rare earth bearing mineral. Such minerals may be used in mining operations long ago but still remains of REEs have been found in the study area. The average concentration of LREEs and HREEs in roots found were 12.85 and 7.70 μg g^{-1} respectively given in **Table 6.4.** A study reported by Brioschi et al (2013) show high absorbance of REEs by the roots of plants from the soil. Uptake capacity of REEs is not only controlled by the plant itself but other factors such as soil speciation, concentration, pH and redox potential are also involved (Brioschi et al., 2013).

Albizia myriophillia has long been known for its medicinal properties and largely applied in Thai herbal medicines (Joycharat et al., 2013). For the first time, this plant was also evaluated for its REEs bioavailability. Stem, leaves and flower of this plant were analyzed and results are shown in **Figure 6.5 (b)** and **Table 6.4.** The stem of the *Albizia myriophillia* contains the highest amount of Ce (42.25 μg g^{-1}) followed by La (35.66 μg g^{-1}). Gd and Sc were also in significant quantities (20 μg g^{-1} and 19.65 μg g^{-1}) respectively. Yttrium (Y) was present in 11.22 μg g^{-1} concentration. The Nd is also a constituent of monazite mineral found in 12.33 μg g^{-1} concentrations. The Nd has been used for a long time in magnets and other agricultural industries in making fertilizers. Pr in the stem was also in considerable amount (11.05 μg g^{-1}).

Table 6.4: Mean concentrations(µg g^{-1}) of REEs in plant parts analyzed along with LREEs and HREEs.

REEs	*Hyptis suaveolens L. (P9)*			*Albizia myriophillia (P10)*			*Eleusine indica L. (P11)*		
	tolerant			**hyperaccumulator**			**hyperaccumulator**		
	(Root)	**(Stem)**	**(Leaves)**	**(Stem)**	**(Leaves)**	**(Flower)**	**(Root)**	**(Leaves)**	**(Flower)**
Sc	12.65 ± 0.82	2.25 ± 1.14	4.82 ± 1.14	19.65 ± 1.35	26.78 ± 1.16	4.62 ± 1.21	45.98 ± 0.73	82.22 ± 0.89	10.12 ± 1.07
Y	11.11 ± 0.61	6.55 ± 1.15	5.28 ± 1.0	11.12 ± 0.98	16.96 ± 0.90	3.55 ± 1.16	22.56 ± 0.75	53.05 ± 1.21	9.65 ± 1.04
La	16.21 ± 0.70	3.17 ± 0.78	6.97 ± 1.1	35.66 ± 1.08	22.34 ± 1.2	5.15 ± 0.82	31.18 ± 0.88	52.66 ± 1.24	10.28 ± 0.95
Ce	17.9 ± 1.08	1.3 ± 1.22	7.16 ± 0.88	42.25 ± 0.99	31.54 ± 1.28	6.96 ± 0.84	62.01 ± 1.07	115.52 ± 0.96	16.52 ± 1.19
Pr	9.67 ± 1.04	2.11 ± 1.16	5.96 ± 0.96	11.05 ± 1.05	15.22 ± 1.31	2.02 ± 1.28	16.85 ± 0.96	25.15 ± 1.12	2.33 ± 1.25
Nd	17.47 ± 1.26	2.22 ± 0.86	6.85 ± 0.83	12.33 ± 1.23	16.85 ± 0.93	1.11 ± 1.09	25.65 ± 1.58	26.33 ± 1.07	1.95 ± 0.87
Eu	6.93± 1.1	1.58 ± 1.18	7.98 ± 1.2	7.95 ± 1.05	8.7 ± 0.95	0.69 ± 0.76	13.31 ± 1.25	8.53 ± 0.96	0.28 ± 0.65
Gd	10.81 ± 1.23	4.12 ± 1.01	5.32 ± 1.13	20.00 ± 1.11	19.77 ± 1.44	3.44 ± 1.05	31.08± 1.28	51.92± 1.32	7.3± 0.82
LREEs	12.85 ± 1.08	2.29± 1.63	6.29± 1.24	18.85± 0.58	18.77 ± 1.65	3.32 ± 1.15	30.80± 1.08	49.96 ± 1.56	7.16 ± 0.95
Tb	9.2 ± 0.97	2.65 ± 0.87	6.24 ± 1.33	6.92 ± 0.84	10.95 ± 0.88	3.55 ± 1.01	15.08 ± 0.89	32.63± 1.08	2.65 ± 1.12
Dy	7.21 ± 1.07	3.43 ± 1.1	5.61 ± 0.95	9.41 ± 0.88	12.14 ± 1.08	1.88 ± 0.87	18.61 ± 0.68	46.01 ± 0.85	4.95 ± 0.75
Ho	6.48 ± 0.85	1.21 ± 1.38	7.11 ± 1.19	4.63 ± 0.85	7.22 ± 0.81	1.59 ± 1.03	16.22 ± 0.95	12.93 ± 0.89	1.17 ± 1.15
Er	6.95 ± 1.22	3.58 ± 1.29	4.34 ± 1.46	7.55 ± 0.98	11.35 ± 1.12	2.65 ± 0.83	10.25 ± 1.11	23.95 ± 0.86	3.33 ± 1.16
Tm	8.42 ± 0.98	0.69 ± 1.38	2.98 ± 1.34	9.69 ± 1.27	7.47± 1.18	3.77 ± 1.15	12.35 ± 1.23	8.32 ± 0.98	1.05 ± 1.35
Yb	9.56 ± 1.24	1.92 ± 0.94	6.62 ± 1.11	14.69 ± 0.97	12.15 ± 1.23	4.25 ± 1.22	23.66 ± 1.35	37.69 ± 1.16	4.55 ± 1.04
Lu	6.11 ± 1.37	1.77 ± 1.16	4.35 ± 1.41	5.05 ± 0.94	2.11 ± 1.38	0.42 ± 0.78	7.58 ± 0.91	2.11 ± 1.32	0.69 ± 1.14
HREs	7.70± 1.11	2.18 ± 0.45	5.32± 1.33	8.28 ± 1.44	9.06 ± 0.36	2.59 ± 1.87	14.82 ± 2.05	23.38 ± 0.88	2.63± 1.35

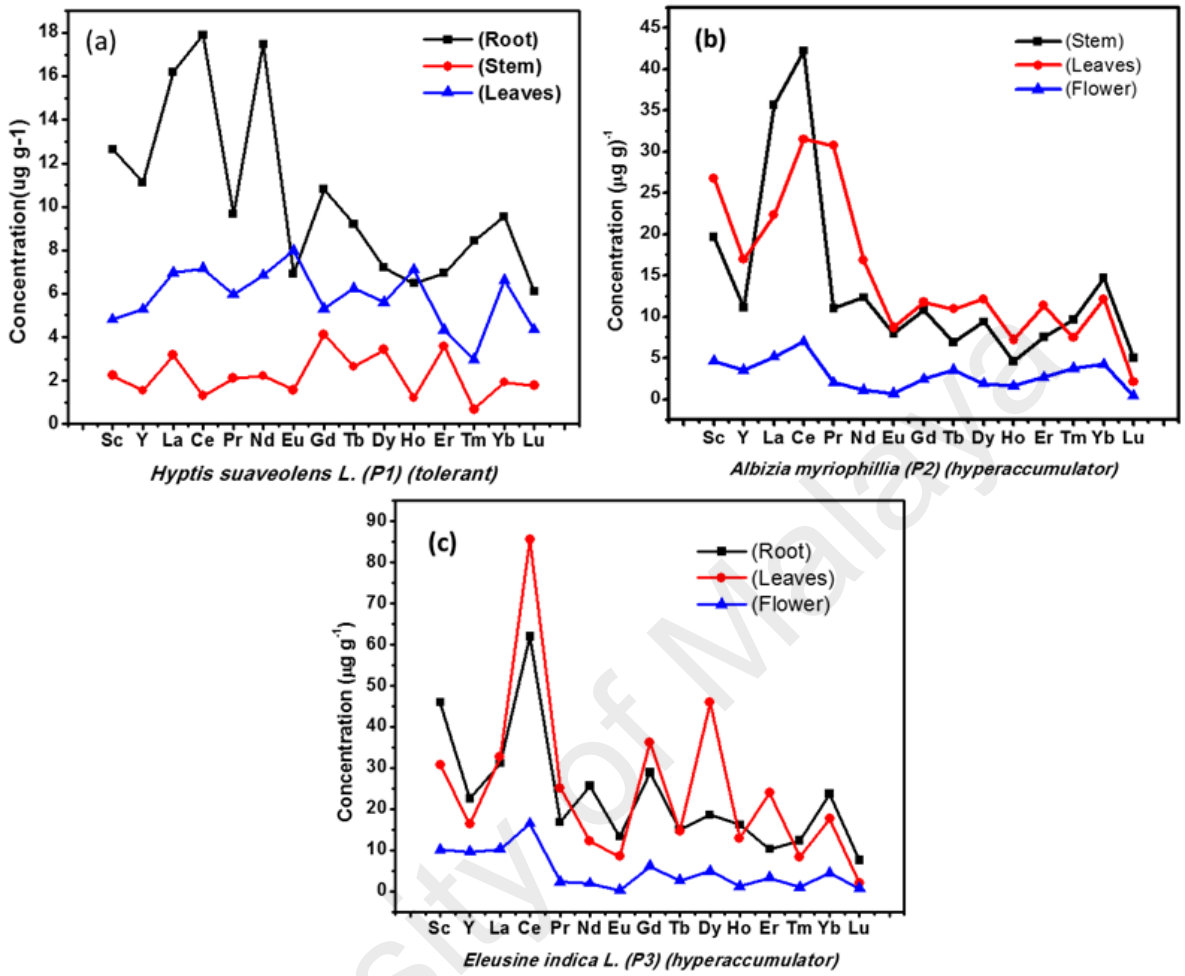


Figure 6.6: Concentration of rare earth elements (REEs) in wild plants collected from the study area.

After analyzing the data for REEs it was found that LREEs are more accumulated by the plant than HREEs. LREEs have more potential mobility in the soil than heavy rare earth elements (HREEs). The leaves of the *Albizia myriophillia* were found hyper accumulator for nearly all REEs **(Figure 6.5 b).** Ce was in maximum concentration (31.54 μg g^{-1}) accumulated in the leaves. Sc was the second rare earth element in higher concentration 26.78 μg g^{-1} followed by La (22.34 μg g^{-1}) while Nd, Gd, Y, Pr and Eu were also investigated in concentrations 16.85, 19.77, 16.96, 15.22 and 8.7 μg g^{-1} respectively.

Among HREEs Tb, Dy, Ho, Er, Tm, Yb and Lu were also in significant quantities with 10.95, 12.14, 7.22, 11.35, 7.47, 12.15 and 2.11 μg g^{-1} respectively. Average LREEs were found in 11.75 μg g^{-1} while HREEs were 9.39 μg g^{-1}. Flower of this plant has been extensively used in the medical purposed for medicines. Flower was found to accumulate and deposit with less REEs. The maximum amount was found for Ce (6.96 μg g^{-1}).

Eleusine indica L, another medicinal plant widely applied in herbal treatments. In the present investigation, this plant was found in the accumulation of REEs. Previous studies reported by Adallah et al (2012) and Tela et al (2012) indicate the bioaccumulation of metals by the *Eleusine indica L.* (Abdallah et al., 2012, Tela et al., 2012). Anh et al (2011) reported the very high uptake capacity of Pb (0.15-0.65 %) and Zn (0.22-1.6 %) in the roots of *Eleusine indica L* (Anh et al., 2011).

The results from current study indicate that compared to other plant species analyzed *Eleusine indica L*, absorb more REEs from the soil through the roots and transport to other aerial parts as well shown in **Figure 6.5 (c).** Ce in the roots of this plant was highest (62.01 μg g^{-1}) of all the roots. Sc was also found associated with roots in 45.98 μg g^{-1} concentration. Concentration of La was observed 31.18μg/g which was about the double

in the roots of *Hyptis suaveolens L.* Nd was also accumulated and taken up from the soil in considerable quantity (25.65 μg g^{-1}). Uptake capacity of Nd found approximately the same in all plants. Y, Pr, Eu and Gd were 22.56, 16.85, 13.31 and 31.08 μg g^{-1}, respectively. HREEs were also found in much higher concentrations compared to other plants given in **Figure 6.6** (de Araújo et al., 2012). Tb, Dy, Ho, Er, Tm, Yb and Lu were found in concentration 15.08, 18.61, 16.22, 10.25, 12.35, 23.66 and 7.58 μg g^{-1}, respectively.

REEs in the leaves of *Eleusine indica L* found enriched with Ce (115.52 μg g^{-1}) compared to the leaves of other medicinal plants. Such high concentration indicates the ability of the Ce to get absorbed by the roots and transfer to plants (Ichihashi et al., 1992). Another reason for higher deposition of REEs could be the atmospheric deposition on the surface of leaves. Sc, Y, La, Pr, Nd, Eu and Gd were 82.22, 53.05, 52.66, 25.15, 26.33, 8.53 and 51.92 μg g^{-1}, respectively. HREEs were in varying concentrations. Tb, Dy, Ho, Er, Tm, Yb and Lu were found in concentrations 32.63, 46.01, 12.93, 23.95, 8.32, 37.69 and 2.11 μg g^{-1} respectively. Flower of *Eleusine indica L* shows concentration higher than *Albizia myriophillia*. In the flower part of *Eleusine indica L.* Ce was found in maximum concentration (16.52 μg g^{-1}). In the present study, a wide range of variations in the concentration of all REEs has been found in all plant samples analyzed.

The transfer factor (TF), bioconcentration factor (BCF) and bioaccumulation factor (BAF) of rare earth elements (REEs) in different medicinal plants grown on the ex-mining soil were analyzed are given in **Figure 6.7**. Such factors have been widely applied for REEs for many years and considered much more important for evaluating their behaviour in soil-plant system (Ndeda and Manohar, 2014). Sequence of TF, BCF and BAF for REEs was: *Eleusine indica L.> Albizia myriophillia >Hyptis suaveolens L.*

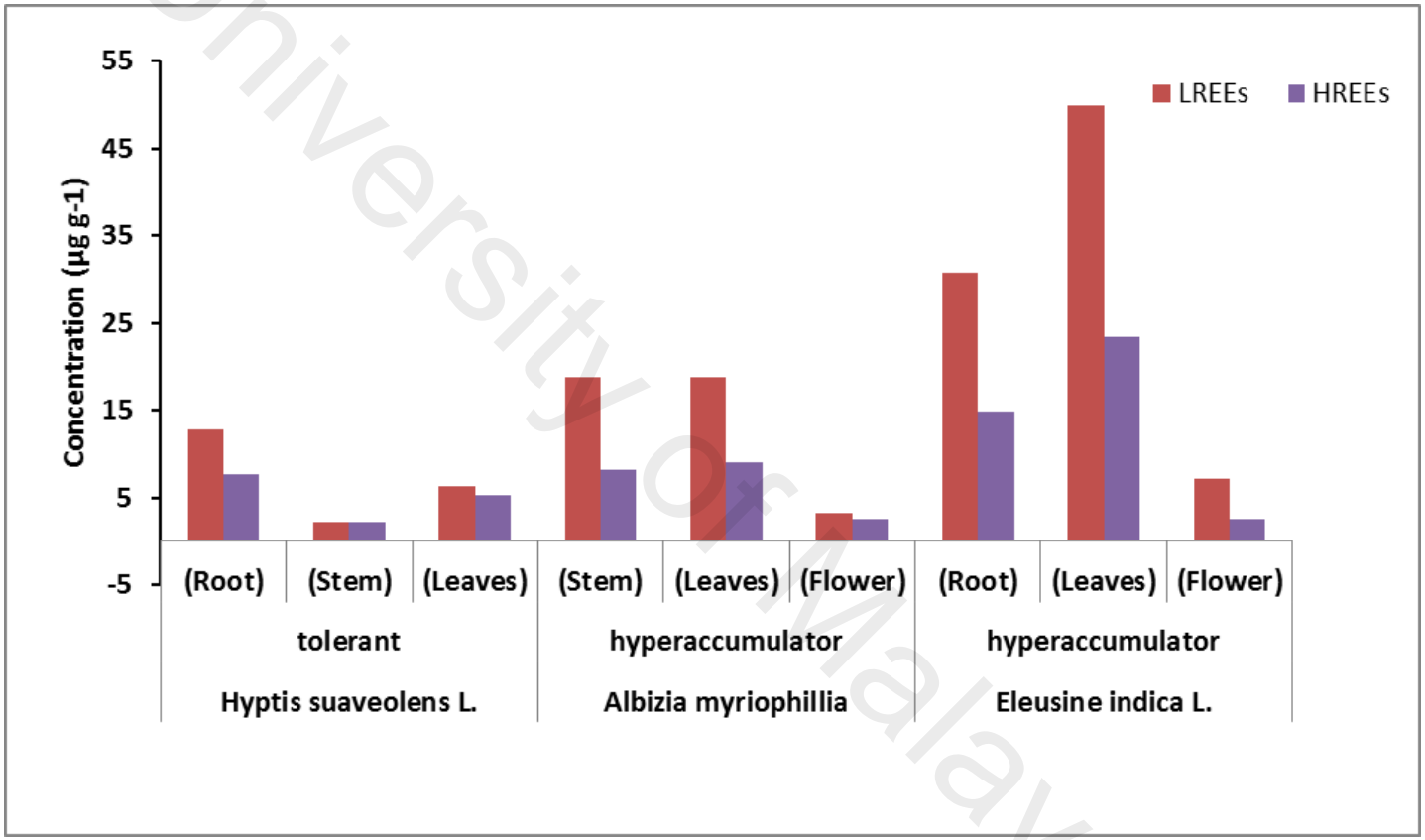


Figure 6.7: The uptake capacity of wild plants for light rare earth elements (LREEs) and heavy rare earth elements (HREEs).

Transfer factor (TF) was highest in *Eleusine indica L*. for Dy (2.47) followed by Y (2.3) and Tb (2.3) whereas Sc, Y, La, Ce, Pr, Nd, Gd, Tb, Er, and Yb have values > 1. In *Albizia myriophillia* most of the LREEs such as Sc, Y, Pr, Nd and Eu have TF> 1. Y was found with TF value of 1.5. Compared to other plant species, REEs in *Hyptis suaveolens L*. do not have TF> 1 suggesting that nearly all rare metals are concentrated into the soil or roots of the plant, but TF< 1 explains the REEs tolerance ability for *Hyptis suaveolens* **(Figure 6.7 a)** . The result suggested that the rare earth metals (REEs) having TF> 1 can be effectively translocated from roots to the shoot and other parts of the plant. Transfer factor is mostly correlated to the mass fraction of metals in the soil and physico-chemical properties. Toxicity of the metals is directly related to their concentration which is correlated to distribution, mobility, transfer to other environments and bioavailability (Ji et al., 2004, Hongbing et al., 2010).

Bioconcentration factor (BCF) was found highest for Ce (2.72) in *Eleusine indica L* and for other REEs was found with greater than 1 such as Sc (1.9), Y (1.2), La (1.2), Gd (1.1), Dy (1.0) and Yb (1). *Albizia myriophillia* also show BCF > 1 for Sc (1.3), La (1.1), Ce (1.5), Gd (1.0), Dy (1.0), Er (1.0) and Yb (1.1) *Hyptis suaveolens* show BCF< 1 for all REEs (**Figure 6.7 b).** Higher BCF values of *Eleusine indica L* and *Albizia myriophillia* may be due to decreased potential of soil water, dilution of rare earth elements (REEs) and precipitation that enhanced the plant growth (Agyarko et al., 2010). Bioavailability of the REEs largely depends on the internal and external environmental factors. Such factors make them hyperaccumulators for REEs and these plants because of their metal uptake capacity can be used for phytoremediation purpose.

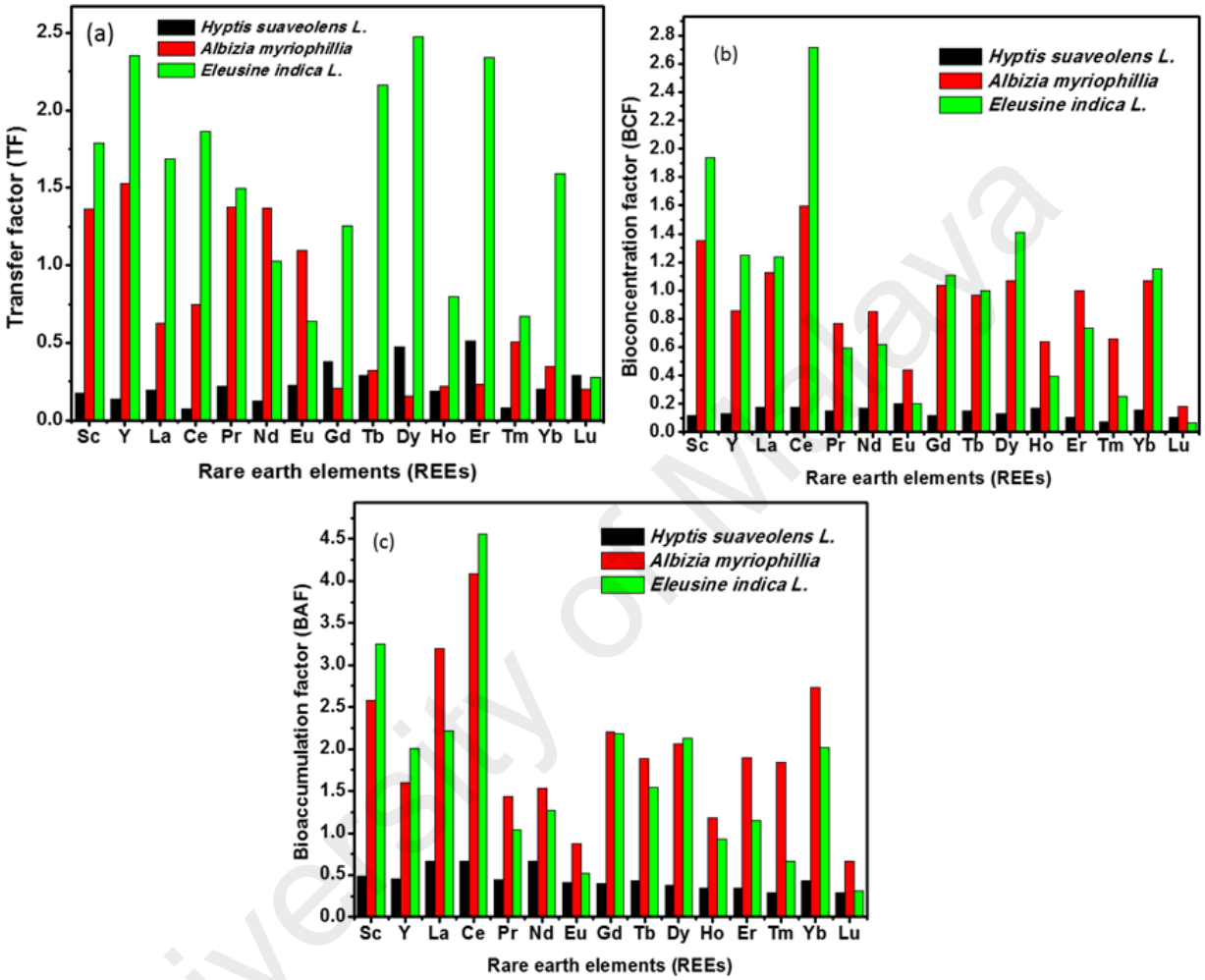


Figure 6.8: Transfer factor (TF), bioconcentration factor (BCF) and bioaccumulation factor (BAF) of wild plants studied for REEs.

Bioaccumulation factor (BAF) of REEs in *Eleusine indica L* and *Albizia myriophillia* was highest for Ce (4.5) and (4.0), respectively. Other REEs in were found with BAF as Sc (3.2), Y (2.0), La (2.2), Pr (1.04), Nd (1.2), Gd (2.1), Tb (1.5), Dy (2.1), Er (1.1) and Yb (2.0) shown in **Figure 6.7 (c)**. *Albizia myriophillia* plant from mining area also shows bioaccumulation capacity for all REEs except Eu and Lu. *Hyptis suaveolens L.* has BAF factor < 1 for all REEs showing same trend as for TF and BCF. Bioaccumulation factor (BAF) decreases with increasing soil rare earth metal concentration (Efroymson et al., 2001, Zhao et al., 2003). Bioaccumulation factor (BAF) for each plant was different according to the nature of the plant and studied parts. Most of the REEs were found to accumulate in the leaves and roots of the studied medicinal plants while the stem and flower show less bioaccumulation.

For the phytoremediation of REEs from soil, an efficient tool for the plant should be higher than 1. In this study, BCF and BAF were > 1 for most of the REEs in *Eleusine indica L* and *Albizia myriophillia* suggesting their high performance in phytoremediation of pollution from soil. From the results, it is represented that all plants show different behaviour for REEs from each other.

6.3 Bioavailability of LREES in *Ricinus communis L.* and unique *Emilia sonchifolia* plants

Ricinus communis L. (Castor bean) is a widely grown plant on mining land because of its high resistance towards metal tolerance, belongs to family Euphorbiaceae. This plant has been previously used for phytoremediation of metals (Olivares et al., 2013). *Ricinus communis L.* has the ability to withstand all types of weather and climatic conditions. Many researchers also found this plant as source of bioenergy rather than as food (Rajkumar & Freitas, 2008). *Emilia sonchifolia* is an annual herb belonging to Astraceae, commonly known as lilac tassel flower and setumbak Merah in Malaysia. This plant has

been previously used as antioxidant, anticancerous and for medicinal purposes (Essien et al., 2009). In this research these species have been evaluated for the first time for light rare earth elements (LREEs) shown in **Figure 6.1**. Beside, their use in food and in medical purpose, the current study focuses on their uptake capacity and bioavailabilitiy of very common and important REEs such as light rare earth elements. These plants were found in the mining areas from different regions. It was very interesting to know their rare metal capacity.

6.3.1 Rare earth elements (REEs) uptake in the soil

Soil samples were analyzed for their physical properties and light rare earth elements (LREEs) and results are given in **Table 6.5.** pH of the soil of *Ricinus communis L*. (P12) was 6 whereas of *Emilia sonchifolia* was less about 5.3. Electrical conductivity values for both the plants found were 52.9 (µS cm^{-1}) and 15.9 (µS cm^{-1}). It was found that the soil where *Ricinus communis L*. was grown contains more metal ions than other plant species.

Table 6.5: Physico-chemical parameters of soil collected and analyzed for LREEs.

Soil Parameters	*Ricinus Communis L.*	*Emilia Sonchifolia*
pH	6.0 ± 0.08	5.3 ± 0.24
EC(µS cm^{-1})	52.9 ± 0.11	15.9 ± 0.31
CEC(cmol kg^{-1})	16.0 ± 0.15	21.0 ± 0.04
MC (%)	8.0 ± 0.44	32.0 ± 0.28
OM (%)	21.0 ± 0.11	12.0 ± 0.15
Sc	44.6 ± 0.04	30.17 ± 0.18
Y	15.5 ± 0.22	35.26 ± 0.65
La	62.88 ± 0.40	55.69 ± 0.36
Ce	74.58 ± 0.05	76.27 ± 0.16
Pr	24.75 ± 0.11	20.65 ± 0.23
Nd	92.6 ± 0.37	80.36 ± 0.59

*all REEs measured in units mg kg^{-1}

Cation exchange capacity (CEC) was 16 cmol kg^{-1} and 21 cmol kg^{-1} for both plant species analyzed. Moisture content was found high for *Emilia sonchifolia* soil but organic matter content was found high in *Ricinus communis L*. Among the LREEs Sc, La, Pr and

Nd were high in the soils of *Ricinus communis L* whereas Y and Ce were abandoned in *Emilia sonchifolia.* Results were confirmed by using SRM values for reference which is shown in **Table 3.4.**

6.3.2 LREEs uptake capacity and bioavailability in plants

Different parts of these plants after being prepared were studied for LREEs. Their concentration varies in different parts of same plants and also compared to other plant specie analyzed. Results obtained have been shown in **Table 6.6** and **Figure 6.8**. For every plant grown in any kind of soil, root play an important role for its growth and nutrition. Root of *Ricinus communis L.* absorb Sc 22.1 (µg g^{-1}), Y 6.7 (µg g^{-1}), La 36.5 (µg g^{-1}), Ce 66.1 (µg g^{-1}), Pr 11.4 (µg g^{-1}) and Nd 35.1 (µg g^{-1}). Leaves of this plant contain Ce (35.5 µg g^{-1}) in highest concentration. La was detected in 25.5 µg g^{-1} while Sc was 18.6 µg g^{-1}.

Table 6.6: Concentrations of LREEs in different parts of plant species analyzed.

Elements	***Ricinus Communis* (Castor) (µg g^{-1})**			***Emilia Sonchifolia* (lilac tassel flower) (µg g^{-1})**		
	Root	**Stem**	**Leaves**	**Root**	**Stem**	**Leaves**
Sc	22.1 ±0.21	15.5 ±0.14	18.6 ±0.05	6.5 ±0.13	2.5 ±0.42	19.5 ± 0.55
Y	6.7 ±0.01	3.5 ± 0.65	6.3 ±0.22	3.2 ±0.11	0.8 ± 0.01	5.2 ± 0.13
La	36.5 ± 0.55	18.1 ± 0.62	25.5 ± 0.28	22.2 ± 0.04	6.9± 0.09	35.5 ± 0.17
Ce	66.1 ± 0.63	12.2 ± 0.59	35.5 ± 0.11	41 ± 0.27	11.5 ± 0.11	48.2 ± 0.22
Pr	11.4 ± 0.05	2.2 ± 0.26	4.6± 0.08	3.4 ± 0.14	1.1 ± 0.04	12.5 ± 0.11
Nd	35.1 ± 0.28	6.5 ± 0.18	20 ± 0.36	16.5 ± 0.25	2.05 ± 0.34	10.6 ± 0.12

This plant is considered as high biomass and has the capability to take up metals from soil. Previous studies show its high uptake capacity for certain metals. This plant is considered as hyperaccumulator for heavy metals (Abreu et al., 2012). In this study it was found for light rare earth elements (LREEs). Roots of *Ricinus communis L.* were high in LREEs represented in **Figure 6.8 (a).** *Emilia sonchifolia* (P13) was also studied

for its rare metal uptake capacity. This plant is a fast growing specie among its family. Ce was high in leaves (48.2 µg g^{-1}) as shown in **Figure 6.8 (b).**

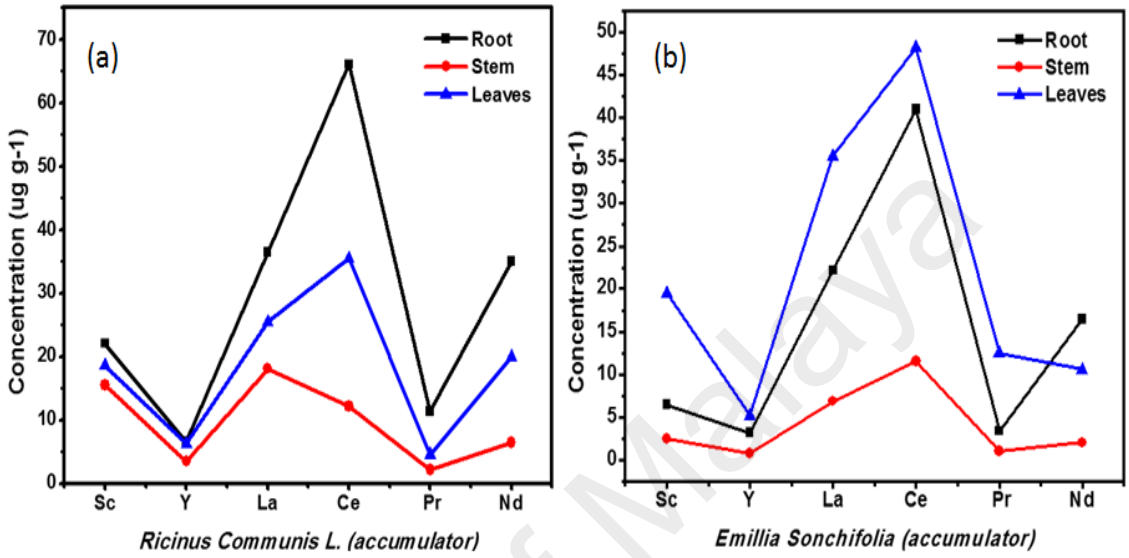


Figure 6.9: Concentration of light rare earth elements (LREEs) in plants stem, root and leaves of (a) *Ricinus Communis L.* root shows greater uptake capacity of LREEs from soil (b) *Emilia Sonchifolia* leaves were found loaded with LREEs.

The transfer factor (TF), bioconcentration factor (BCF) and bioaccumulation factor (BAF) of light rare earth elements (LREEs) in these plants grown on the ex-mining soil were also analyzed. Such factors have been widely applied for REEs for many years and considered much important for evaluating their behaviour in soil-plant system (Ndeda & Manohar, 2014). Transfer factor is mostly correlated to the mass fraction of metals in the soil and physico-chemical properties.

In this study for Ricinus *communis L.* TF factor was found less than 1 which shows the lower transfer of LREEs from roots to the shoots **Figure 6.9 (a).** This is the reason that most of LREEs were concentrated in the roots and acting as accumulator. BCF factor

was also found less than 1. Lower BCF values may be due to increased potential of soil water, dilution of LREEs and low precipitation that decrease the plant growth (Agyarko et al., 2010). BAF factor was > 1 for Y, La and Ce. For the removal of pollutants from the soil and keep it as green it is good having BAF >1 meaning that such plants can be used for phytoremediation.

Emilia sonchifolia (lilac tassel flower) show very low TF from roots to shoots given in **Figure 6.9 (b)**. Most of the LREEs were concentrated in the roots and very less were found in shoots. BCF was also < 1 for all LREEs whereas BAF was > 1 for La and Ce. Comparing the uptake capacity and accumulation behavior it was concluded that most of the REEs were mainly present in the roots while both plants have the capability to accumulate these rare metals in them. Both plant species used in this study were found with considerable amounts of LREEs. Ce, La and Y were mainly found in roots and leaves of the plants.

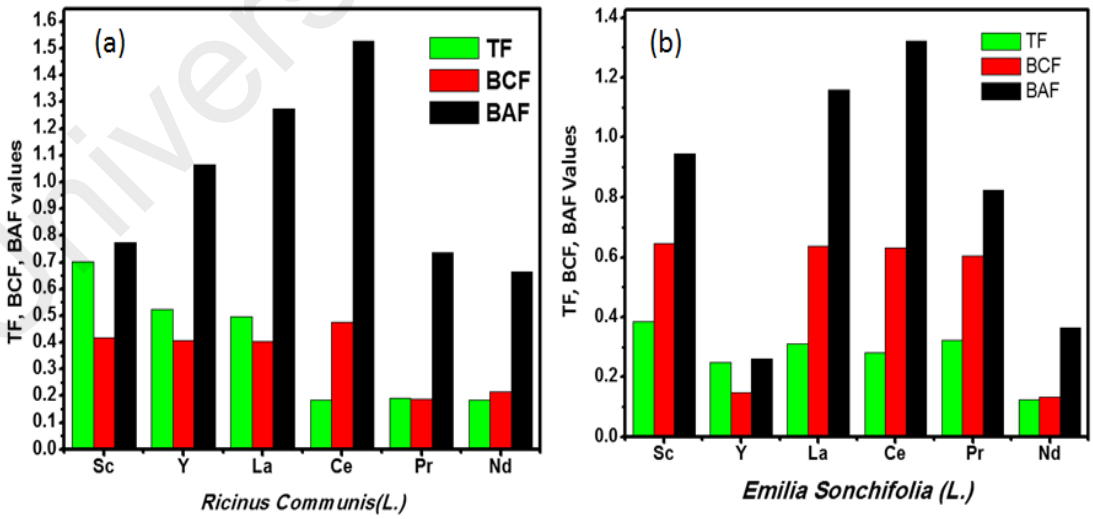


Figure 6.10: Transfer factor (TF), bioconcentration factor (BCF) and bioaccumulation factor (BAF) of (a) *Ricinus Communis L.* and (b) *Emilia sonchifolia* studied for REEs.

Shoots were low in these rare elements. BCF and BAF were > 1 for some elements indicating that these plants can be used for phytoremediation of light rare earth elements from contaminated soil. So far no study has been found previously for REEs in these plants.

Summary

REEs uptake capacity and plant bioavailability has been focused in this chapter. Plants belonging to ex-mining areas were collected and analyzed using their different parts. In this study plants which were commonly found, abundantly found and some unique species on mining land were selected for LREEs evaluation. Different environmental factors such as TF, BCF and BAF were calculated to check their uptake capacity and bioavailabilitiy.

CHAPTER 7: CONCLUSION

The water, sediment, soil and plant collected from the ex-mining area in Kinta valley, Perak were studied for REEs concentration, speciation and bioavailability using ICP-MS as a major elemental technique. This research has confirmed the presence of REEs in the soils of the ex-mining area in Perak, Malaysia. All the REEs except samarium have been detected in the soil samples at different levels. This ex-mining area showed elevated levels of REEs concentration, indicating the impacts of mining and anthropogenic activities that had been stopped years ago. The concentration of Ce in a mining lake water sample was found highest with an average value of 46.50 $\mu g\ g^{-1}$ while Yb and La were found with average values of 18.23 and 17.77 $\mu g\ g^{-1}$, respectively. The decreasing trend of REEs concentration in lake waters was as follows: Ce > Yb > La > Sc > Tm > Y> Er > Dy > Nd > Pr > Gd > Lu > Eu > Ho > Tb. River water also contains average concentrations of Ce, Yb and La with 29.95, 12.66 and 11.51 $\mu g\ g^{-1}$, respectively. In Kinta river water different trend in concentration of REEs compared to mining lake water was found. The order of decreasing concentration trend in Kinta water can be represented as follows: Ce > Yb > La > Tm > Sc > Nd > Er > Pr > Dy > Y > Gd > Lu > Tb > Eu > Ho.

In sediment, La was found in much higher concentration with an average value of 765.8 $mg\ kg^{-1}$. Increase in the pH can leach the REEs from the surface of sediments and disperse them as ions. The decreasing trend of REEs in the sediment samples from ten stations is given as: La > Ce> Dy> Y> Gd > Pr > Sc > Nd > Yb > Er > Tm > Eu >Lu > Ho > Tb. Soil samples analyzed from three different depths showed variations in distribution of REEs in the ex-mining area. pH of the soil ranges from acidic to neutral while CEC and organic matter content were found low. Electrical conductivity was found high in some sampling locations. Sandy deposits were mostly found in the abandoned mining area. In comparison with different depths, an upper layer of the soil was found

enriched with REEs and other two layers having less concentration in general. The current findings also suggest the enrichment of LREEs in all layers of soil than HREEs and sourced from rare earths bearing mineral (e.g. monazite) and previous mining activities in the area.

The REEs decreasing concentration trends in the surface soil (0-20 cm) were found as: Ce > Nd > La > Y> Sc > Gd > Pr> Tb > Yb > Dy >Er > Tm > Eu > Ho > Lu. In the middle soil layer (21-40 cm) terbium (Tb) and promethium (Pr) show trend in different concentration than other elements. The decreasing trend for middle soil for all REEs analyzed can be represented as follows: Ce > Nd > La > Y> Sc > Gd > Tb > Yb > Dy > Pr > Tm > Eu > Er > Ho > Lu. The deeper the soil layer (41-60 cm) REEs show somewhat different distribution. In this layer, yttrium (Y) was found higher in concentration than lanthanum (La) in the surface and middle soil layers. Gd and Er were also found high in concentration than other HREEs. The decreasing trend of REEs in this layer was found as: Ce > Nd > Y > La > Sc > Tb > Yb > Gd > Dy > Pr > Er > Tm > Eu > Ho > Lu.

It can be concluded from the given trends that LREEs are more abundant and have high distribution in the soil than HREEs. The results from the experimental study and statistical data evaluation of the three different soil depths profile clearly define abandoned mines still loaded, depleted and distributed with all the REEs and considered as a major source of major elements such as Ce, La, Nd, Sc, and Y. Moreover, separation of soil samples based on sampling depths into two clusters was made possible by PCA and HCA. The discriminating factors were the concentrations of the rare elements such as La, Ce, Gd, Nd, Tm, Pr, Sc, Er, Eu, Tb, Ho, Lu, Yb, and Dy. Different environmental risk assessment has shown that top soil is much polluted with rare earth, but less polluted in deeper layers. It can conclude from the study that presence of rare earth in the topsoil layer of the mining area is good for it can be remediated by using safe and suitable

methods in order to prevent the environment from harmful effects which now a day's world is bearing.

Speciation study in sediments reveals REEs were abundant in the exchangeable fraction, indicating that these could be easily released to the aquatic environment by making complexes with other ions. In fraction I (AEC), the highest REE found was Y in (46.2 %), in fraction II (Amorphous Fe oxyhydroxide) was Tm (13.1 %), in fraction III (Crystalline Fe oxyhydroxides) was Tb (12.7 %), fraction IV (sulphides & organics) (22.9 %) and in fraction V (silicate & residuals) was La (41.1 %). The average potential mobility of the REEs can be arranged in decreasing order for sediment as follows: Yb> Gd> Y=Dy> Pr> Er> Tm> Eu> Nd>Tb> Sc> Lu> Ce> La. Elevated average potential mobility of Yb (67.3 %) in sediment samples implying that under favorable conditions they can be released to pollute the environment.

Speciation study in soil samples reveals the presence of most of the REEs in the AEC and the residual fraction of sequential extraction with the increase in the percentage of organic matter content with increasing soil depth but subsoil (21-40 cm) found enriched. AEC fraction indicate easy exchanged, removal and co-precipitation of REEs from the soil in the surrounding environment. Surface soil (0-20 cm) was affected and polluted with respect to mining activities while subsoil (21-40 cm) and deeper (41-60 cm) soil was less affected. REEs also evaluated as immobile due to higher percentages in residual fraction. Minor amounts of REEs are associated with crystalline and amorphous Fe oxyhydroxides. All samples from the soil depth profiles in abandoned mines were found rich in LREEs compared to HREEs. Potential mobility indicates REEs ability to transfer to other components of an ecosystem. Fractionation of REEs through speciation in soil depth profile suggest that changes in physico-chemical and geological conditions can cause variations in distribution and potential mobility through soil to other environments.

Potential mobility of REEs in surface soil vary as follows: Sc > Y > Tb > Tm> Yb > Eu > Dy > Lu > Ho > Pr > Er > Nd > Ce > Gd. Middle and deeper soil layer REEs potential mobility varies more than surface soil. Decreasing trends of potential mobility for middle soil can be shown as: La > Nd > Y > Ce > Lu > Tb > Yb > Sc > Er > Gd > Pr > Dy > Eu > Tm > Ho. Deeper soil layers show much variations in potential mobility that may be due to change in physical characteristics such as pH, organic matter content, cation exchange capacity and moisture content. The decreasing order of potential mobility for deeper soil can be represented as: Eu > Pr > Er > Dy > Tm > Yb > Tb > Gd > La > Nd > Ho > Sc > Ce > Lu > Y.

After analyzing the soil and plant samples, it was found that environment of the ex-mining area due to mining activities has been changed in past few decades. High amount of REEs through various transport processes released into the environment, accumulated in different parts of the plants and get bioavailable. The current study indicates most of the plants grown in ex-mining area rich in REEs. Plants belonging to different families indicate most of them hyperaccumulator, some accumulator while others tolerant to REEs uptake from the soil. *Dicranopteris dichotoma., Dicranopteris linearis(Burn) (B), Cyperus distans L., Cyperus rotundus L.* were found as hyperaccumulators and *Dicranopteris linearis(Burn) (A)* and *Cyperus kyllingia Rottb.*as accumulator while *Melastoma malabathricum L.* and as hyper tolerant and *Cyperus difformis Rottb.*as tolerant. Order of uptake capacity for REEs for all plant species was found as follows: roots> leaves> stem> flower. LREEs were found more in studying plants than HREEs. Bioavailability of LREEs in the soil and plants, mostly affected by the pH that plays a key role in their behavior in the environment. Translocation factor (TF), bioconcentration factor (BCF) and bioaccumulation factor (BAF) were also calculated. TF was found more than 1 in *Cyperus kyllingia Rottb* and *Cyperus distans L.* BCF was found highest in *Cyperus distans L*. (P7) and higher for all other plants. Bioaccumulation factor (BAF)

was highest in *Cyperus rotundus L.* describing much uptake capacity and bioavailability of the plant to REEs from the soil. All other plants also found with the high amount of BAF. The increase in these accumulation factors reveals the harmful effects of REEs in the environment and toxicity. The results also conclude that most plant species grown in mining area have the ability to accumulate and transfer REEs. If such plants are removed from deep down the soil, this could be a good phytoremediators for the removal of REEs from the ex-mining area soil.

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LIST OF PUBLICATIONS AND PAPERS PRESENTED

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2- Khan, A., Yusoff, I., Abu Bakar, N. K., Abu Bakar, A. F., Alias, Y., & Mispan, M. (2017). Accumulation, Uptake and Bioavailability of Rare Earth Elements (REEs) in Soil Grown Plants from Ex-Mining Area in Perak, Malaysia. *Applied Ecology and Environmental Research*, *15*(3), 117-133.

3- Khan, A. M., Behkami, S., Yusoff, I., Zain, S. B. M., Bakar, N. K. A., Bakar, A. F. A., & Alias, Y. (2017). Geochemical characteristics of rare earth elements in different types of soil: A chemometric approach. *Chemosphere*. *184*, 673-678.

4- Khan, A. M., Bakar, N. K. A., Bakar, A. F. A., & Ashraf, M. A. (2016). Chemical speciation and bioavailability of rare earth elements (REEs) in the ecosystem: a review. *Environmental Science and Pollution Research*, 1-26.

5- Khan, A. M., Yusoff, I., Bakar, N. K. A., Bakar, A. F. A., & Alias, Y. (2016). Evaluation Of Light rare earth elements (LREEs) in castor oil and lilac tassel flower plant grown in contaminated soil from abandoned mines in Perak, Malaysia *(2016 Postgraduate Symposium for Environmental Engineering Technology).*